4. Industrial Processes

Greenhouse gas emissions are produced as a by-product of various non-energy-related industrial activities. That is, these emissions are produced from an industrial process itself and are not directly a result of energy consumed during the process. For example, raw materials can be chemically transformed from one state to another. This transformation can result in the release of greenhouse gases such as carbon dioxide (CO_2), methane (CH_4), or nitrous oxide (N_2O). The processes addressed in this chapter include iron and steel production, cement manufacture, ammonia manufacture and urea application, lime manufacture, limestone and dolomite use (e.g., flux stone, flue gas desulfurization, and glass manufacturing), soda ash manufacture and use, titanium dioxide production, phosphoric acid production, ferroalloy production, CO_2 consumption, aluminum production, petrochemical production, silicon carbide production, nitric acid production, and adipic acid production (see Figure 4-1).

Figure 4-1: 2003 Industrial Processes Chapter Greenhouse Gas Sources

In addition to the three greenhouse gases listed above, there are also industrial sources of man-made fluorinated compounds called hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and sulfur hexafluoride (SF_6). The present contribution of these gases to the radiative forcing effect of all anthropogenic greenhouse gases is small; however, because of their extremely long lifetimes, many of them will continue to accumulate in the atmosphere as long as emissions continue. In addition, many of these gases have high global warming potentials; SF_6 is the most potent greenhouse gas the IPCC has evaluated. Usage of HFCs for the substitution of ozone depleting substances is growing rapidly, as they are the primary substitutes for ozone depleting substances (ODSs), which are being phased-out under the *Montreal Protocol on Substances that Deplete the Ozone Layer*. In addition to ODS substitutes, HFCs, PFCs, SF_6, and other fluorinated compounds are employed and emitted by a number of other industrial sources in the United States. These industries include aluminum production, HCFC-22 production, semiconductor manufacture, electric power transmission and distribution, and magnesium metal production and processing.

In 2003, industrial processes generated emissions of 308.6 teragrams of CO_2 equivalent (Tg CO_2 Eq.), or 4.5 percent of total U.S. greenhouse gas emissions. Carbon dioxide emissions from all industrial processes were 147.2 Tg CO_2 Eq. (147,172 Gg) in 2003. This amount accounted for only 2.5 percent of national CO_2 emissions. Methane emissions from petrochemical, silicon carbide, and iron and steel production resulted in emissions of approximately 2.5 Tg CO_2 Eq. (121 Gg) in 2003, which was 0.5 percent of U.S. CH_4 emissions. Nitrous oxide emissions from adipic acid and nitric acid production were 21.8 Tg CO_2 Eq. (71 Gg) in 2003, or 5.8 percent of total U.S. N_2O emissions. In 2003, combined emissions of HFCs, PFCs and SF_6 totaled 137.0 Tg CO_2 Eq. Overall, emissions from industrial processes increased by 2.9 percent from 1990 to 2003 despite decreases in emissions from several industrial processes, such as iron and steel, electrical transmission and distribution, HCFC-22 production, and aluminum production. The increase in overall emissions was driven by a rise in the emissions originating from cement manufacture and, primarily, the emissions from the use of substitutes for ozone depleting substances.

Table 4-1 summarizes emissions for the Industrial Processes chapter in units of Tg CO_2 Eq., while unweighted native gas emissions in gigagrams (Gg) are provided in Table 4-2.

Table 4-1: Emissions from Industrial Processes (Tg CO_2 Eq.)

Gas/Source	1990	1997	1998	1999	2000	2001	2002	2003
CO_2	**173.1**	**170.9**	**169.4**	**165.9**	**164.7**	**151.8**	**151.5**	**147.2**
Iron and Steel Production	85.4	71.9	67.4	64.4	65.7	58.9	55.1	53.8
Cement Manufacture	33.3	38.3	39.2	40.0	41.2	41.4	42.9	43.0
Ammonia Manufacture & Urea Application	19.3	20.7	21.9	20.6	19.6	16.7	18.6	15.6
Lime Manufacture	11.2	13.7	13.9	13.5	13.3	12.8	12.3	13.0
Limestone and Dolomite Use	5.5	7.2	7.4	8.1	6.0	5.7	5.9	4.7
Aluminum Production	6.3	5.6	5.8	5.9	5.7	4.1	4.2	4.2

Soda Ash Manufacture and Consumption	4.1	4.4	4.3	4.2	4.2	4.1	4.1	4.1
Petrochemical Production	2.2	2.9	3.0	3.1	3.0	2.8	2.9	2.8
Titanium Dioxide Production	1.3	1.8	1.8	1.9	1.9	1.9	2.0	2.0
Phosphoric Acid Production	1.5	1.5	1.6	1.5	1.4	1.3	1.3	1.4
Ferroalloy Production	2.0	2.0	2.0	2.0	1.7	1.3	1.2	1.4
Carbon Dioxide Consumption	0.9	0.8	0.9	0.8	1.0	0.8	1.0	1.3
CH_4	**2.5**	**2.9**	**2.9**	**2.9**	**2.9**	**2.5**	**2.5**	**2.5**
Petrochemical Production	1.2	1.6	1.7	1.7	1.7	1.4	1.5	1.5
Iron and Steel Production	1.3	1.3	1.2	1.2	1.2	1.1	1.0	1.0
Silicon Carbide Production	+	+	+	+	+	+	+	+
N_2O	**33.0**	**31.5**	**26.9**	**25.6**	**25.6**	**20.8**	**23.1**	**21.8**
Nitric Acid Production	17.8	21.2	20.9	20.1	19.6	15.9	17.2	15.8
Adipic Acid Production	15.2	10.3	6.0	5.5	6.0	4.9	5.9	6.0
HFCs, PFCs, and SF_6	**91.2**	**121.7**	**135.7**	**134.8**	**138.9**	**129.5**	**138.3**	**137.0**
Substitution of Ozone Depleting Substances	0.4	46.5	56.6	65.8	75.0	83.3	91.5	99.5
HCFC-22 Production	35.0	30.0	40.1	30.4	29.8	19.8	19.8	12.3
Electrical Transmission and Distribution	29.2	21.7	17.1	16.4	15.6	15.4	14.7	14.1
Aluminum Production	18.3	11.0	9.1	9.0	9.0	4.0	5.2	3.8
Semiconductor Manufacture	2.9	6.3	7.1	7.2	6.3	4.5	4.4	4.3
Magnesium Production and Processing	5.4	6.3	5.8	6.0	3.2	2.6	2.6	3.0
Total	**299.9**	**327.1**	**334.9**	**329.2**	**332.1**	**304.7**	**315.4**	**308.6**

+ Does not exceed 0.05 Tg CO_2 Eq.
Note: Totals may not sum due to independent rounding.

Table 4-2: Emissions from Industrial Processes (Gg)

Gas/Source	1990	1997	1998	1999	2000	2001	2002	2003
CO_2	**173,122**	**170,884**	**169,425**	**165,908**	**164,657**	**151,835**	**151,506**	**147,172**
Iron and Steel Production	85,413	71,863	67,428	64,376	65,693	58,887	55,082	53,763
Cement Manufacture	33,278	38,323	39,218	39,991	41,190	41,357	42,898	43,030
Ammonia Manufacture & Urea Application	19,306	20,650	21,934	20,615	19,616	16,719	18,571	15,560
Lime Manufacture	11,238	13,685	13,914	13,466	13,315	12,823	12,304	12,983
Limestone and Dolomite Use	5,533	7,242	7,449	8,057	5,959	5,733	5,885	4,720
Aluminum Production	6,315	5,621	5,792	5,895	5,723	4,114	4,220	4,219
Soda Ash Manufacture and Consumption	4,141	4,354	4,325	4,217	4,181	4,147	4,139	4,082
Petrochemical Production	2,221	2,919	3,015	3,054	3,004	2,787	2,857	2,777
Titanium Dioxide Production	1,308	1,836	1,819	1,853	1,918	1,857	1,997	2,013
Phosphoric Acid Production	1,529	1,544	1,593	1,539	1,382	1,264	1,338	1,382
Ferroalloy Production	1,980	2,038	2,027	1,996	1,719	1,329	1,237	1,374
Carbon Dioxide Consumption	860	808	912	849	957	818	978	1,267
CH_4	**120**	**139**	**138**	**138**	**138**	**119**	**120**	**121**
Petrochemical Production	56	78	80	81	80	68	72	72
Iron and Steel Production	63	60	57	56	57	51	48	49
Silicon Carbide Production	1	1	1	1	1	+	+	+
N_2O	**107**	**102**	**87**	**83**	**83**	**67**	**75**	**70**
Nitric Acid Production	58	68	67	65	63	51	56	51
Adipic Acid Production	49	33	19	18	19	16	19	19
HFCs, PFCs, and SF_6	**M**	**M**	**M**	**M**	**M**	**M**	**M**	**M**
Substitution of Ozone Depleting Substances	M	M	M	M	M	M	M	M
HCFC-22 Production[a]	3	3	3	3	3	2	2	1
Electrical Transmission and Distribution[b]	1	1	1	1	1	1	1	1
Aluminum Production	M	M	M	M	M	M	M	M

Semiconductor Manufacture	M	M	M	M	M	M	M	M
Magnesium Production and Processing[b]	+	+	+	+	+	+	+	+
NO_x	**591**	**629**	**637**	**595**	**626**	**656**	**630**	**648**
CO	**4,124**	**3,153**	**3,163**	**2,156**	**2,217**	**2,339**	**2,308**	**2,431**
NMVOCs	**2,426**	**2,038**	**2,047**	**1,813**	**1,773**	**1,769**	**1,725**	**1,711**

+ Does not exceed 0.5 Gg
M (Mixture of gases)
[a] HFC-23 emitted
[b] SF_6 emitted
Note: Totals may not sum due to independent rounding.

In order to ensure the quality of the emission estimates from industrial processes, Tier 1 procedures and checks have been performed on all industrial process sources. If performed, Tier 2 procedures focused on the emission factor and activity data sources and methodology used for estimating emissions procedures, and will be described within the QA/QC and Verification Discussion of that source description. In addition to the national QA/QC plan, a more detailed plan was developed specifically for the CO2 and CH4 industrial processes sources. This plan was based on the U.S. strategy, but was tailored to include specific procedures recommended for these sources.

The general method employed to estimate emissions for industrial processes, as recommended by the Intergovernmental Panel on Climate Change (IPCC), involves multiplying production data (or activity data) for each process by an emission factor per unit of production. The uncertainty of the emission estimates is therefore generally a function of a combination of the uncertainties surrounding the production and emission factor variables. Uncertainty of activity data and the associated probability density functions for industrial processes CO_2 sources were estimated based on expert assessment of available qualitative and quantitative information. Uncertainty estimates and probability density functions for the emission factors used to calculate emissions from this source were devised based on IPCC recommendations.

Activity data is obtained through a survey of manufacturers conducted by various organizations (specified within each source); the uncertainty of the activity data is a function of the reliability of plant-level production data and is influenced by the completeness of the survey response. The emission factors used were either derived using calculations that assume precise and efficient chemical reactions, or were based upon empirical data in published references. As a result, uncertainties in the emission coefficients can be attributed to, among other things, inefficiencies in the chemical reactions associated with each production process or to the use of empirically-derived emission factors that are biased; therefore, they may not represent U.S. national averages. Additional assumptions are described within each source.

The uncertainty analysis performed to quantify uncertainties associated with the 2003 inventory estimates from industrial processes continues a multi-year process for developing credible quantitative uncertainty estimates for these source categories using the IPCC Tier 2 approach. As the process continues, the type and the characteristics of the actual probability density functions underlying the input variables are identified and better characterized (resulting in development of more reliable inputs for the model, including accurate characterization of correlation between variables), based primarily on expert elicitation. Accordingly, the quantitative uncertainty estimates reported in this section should be considered illustrative and as iterations of ongoing efforts to produce accurate uncertainty estimates. The correlation among data used for estimating emissions for different sources can influence the uncertainty analysis of each individual source. While the uncertainty analysis recognizes very significant connections among sources, a more comprehensive approach that accounts for all linkages will be identified as the uncertainty analysis moves forward.

4.1. Iron and Steel Production (IPCC Source Category 2C1)

In addition to being an energy intensive process, the production of iron and steel also generates process-related emissions of CO_2 and CH_4. Iron is produced by first reducing iron oxide (iron ore) with metallurgical coke in a blast furnace to produce pig iron (impure iron containing about 3 to 5 percent carbon by weight). Metallurgical coke is manufactured in a coke plant using coking coal as a raw material. Iron may be introduced into the blast furnace in the form of raw iron ore, pellets, briquettes, or sinter. Pig iron (containing about 0.4 percent carbon by weight) is used as a raw material in the production of steel. Pig iron is also used as a raw material in the production of iron products in foundries. The pig iron production process produces CO_2 emissions and fugitive CH_4 emissions.

The production of metallurgical coke from coking coal and the consumption of the metallurgical coke used as a reducing agent in the blast furnace are considered in the inventory to be non-energy (industrial) processes, not energy (combustion) processes. Coal coke is produced by heating coking coal in a coke oven in a low-oxygen environment. The process drives off the volatile components of the coking coal and produces coal coke. Coke oven gas and coal tar are carbon by-products of the coke manufacturing process. Coke oven gas is generally burned as a fuel within the steel mill. Coal tar is used as a raw material to produce anodes used for primary aluminum production and other electrolytic processes, and also used in the production of other coal tar products. The coke production process produces CO_2 emissions and fugitive CH_4 emissions.

Sintering is a thermal process by which fine iron-bearing particles, such as air emission control system dust, are baked, which causes the material to agglomerate into roughly one-inch pellets that are then recharged into the blast furnace for pig iron production. Iron ore particles may also be formed into larger pellets or briquettes by mechanical means, and then agglomerated by heating prior to being charged into the blast furnace. The sintering process produces CO_2 emissions and fugitive CH_4 emissions.

The metallurgical coke is a reducing agent in the blast furnace. Carbon dioxide is produced as the metallurgical coke used in the blast furnace process is oxidized. Steel (containing less than 2 percent carbon by weight) is produced from pig iron in a variety of specialized steel making furnaces. The majority of CO_2 emissions from the iron and steel process come from the use of coke in the production of pig iron, with smaller amounts evolving from the removal of carbon from pig iron used to produce steel. Some carbon is also stored in the finished iron and steel products.

Emissions of CO_2 and CH_4 from iron and steel production in 2003 were 53.8 Tg CO_2 Eq. (53,763 Gg) and 1.0 Tg CO_2 Eq. (48.7 Gg), respectively (see Table 4-3 and Table 4-4). Emissions have fluctuated significantly from 1990 to 2003 due to changes in domestic economic conditions and changes in product imports and exports. In 2003, domestic production of pig iron and coal coke increased by 2.2 and 2.4 percent, respectively. Despite these increases, domestic pig iron and coke production have declined since the 1990s. Pig iron production in 2003 was 15 percent lower than in 2000 and 19 percent below 1995 levels. Coke production in 2003 was 17 percent lower than in 2000 and 38 percent below 1990 levels. A slowdown in the domestic and worldwide economy and the availability of low-priced imports limit growth in domestic production (USGS 2002).

Table 4-3: CO_2 and CH_4 Emissions from Iron and Steel Production (Tg CO_2 Eq.)

Year	**1990**		**1997**	**1998**	**1999**	**2000**	**2001**	**2002**	**2003**
CO_2	85.4		71.9	67.4	64.4	65.7	58.9	55.1	53.8
CH_4	1.3		1.3	1.2	1.2	1.2	1.1	1.0	1.0
Total	**86.7**		**73.1**	**68.6**	**65.5**	**66.9**	**60.1**	**56.1**	**54.8**

Table 4-4: CO_2 and CH_4 Emissions from Iron and Steel Production (Gg)

Year	**1990**		**1997**	**1998**	**1999**	**2000**	**2001**	**2002**	**2003**
CO_2	85,413		71,863	67,428	64,376	65,693	58,887	55,082	53,763
CH_4	63		60	57	56	58	51	48	49

Methodology

Since coke is consumed as a reducing agent during the manufacture of pig iron, the corresponding quantity of coal consumed during coking operations was identified. This quantity of coal is considered a non-energy use. Data were also collected on the amount of imported coke consumed in the blast furnace process. These data were converted to their energy equivalents. The carbon content of the combusted coal and imported coke was estimated by multiplying their energy consumption by material specific carbon-content coefficients. The carbon content coefficients used are presented in Annex 2.1.

Emissions from the re-use of scrap steel and imported pig iron in the steel production process were calculated by assuming that all the associated carbon-content of these materials are released during combustion. Steel has an associated carbon-content of approximately 0.4 percent, while pig iron is assumed to contain 4 percent carbon by weight.

Emissions from carbon anodes, used during the production of steel in electric arc furnaces (EAF), were also estimated. Emissions of CO_2 were calculated by multiplying the annual production of steel in electric arc furnaces by an emission factor (4.4 kg CO_2/ton $steel_{EAF}$). It was assumed that the carbon anodes used in the production of steel in electric arc furnaces are composed of 80 percent petroleum coke and 20 percent coal tar pitch (DOE 1997). Since coal tar pitch is a by-product of the coking process and its carbon-related emissions have already been accounted for earlier in the iron and steel emissions calculation as part of the coking process, the emission factor was reduced by 20 percent to avoid double counting. Additionally, emissions from the coal tar pitch component of carbon anodes consumed during the production of aluminum, which are accounted for in the aluminum production section of this chapter, have been subtracted from the total coal tar emissions that were calculated above.

Carbon storage was accounted for by assuming that all domestically manufactured steel had a carbon content of 0.4 percent. Furthermore, any pig iron that was not consumed during steel production, but fabricated into finished iron products, was assumed to have a by-weight carbon content of 4 percent.

The production processes for coal coke, sinter, and pig iron result in fugitive emissions of CH_4, which are emitted via leaks in the production equipment rather than through the emission stacks or vents of the production plants. The fugitive emissions were calculated by applying emission factors taken from the *1996 IPCC Guidelines* (IPCC/UNEP/OECD/IEA 1997) (see Table 4-5) to annual domestic production data for coal coke, sinter, and pig iron.

Table 4-5: CH_4 Emission Factors for Coal Coke, Sinter, and Pig Iron Production (g/kg)

Material Produced	g CH_4/kg produced
Coal Coke	0.5
Pig Iron	0.9
Sinter	0.5

Source: IPCC/UNEP/OECD/IEA 1997

Data relating to the amount of coal consumed at coke plants, for the production of coke for domestic consumption in blast furnaces, as well as the quantity of coke imported for iron production were taken from the Energy Information Administration (EIA), *Quarterly Coal Report* January through December 2003 (EIA 2004); *U.S. Coal Domestic and International Issues* (EIA 2001); *Mineral Yearbook: Iron and Steel* (USGS 1993, 1995a, 1997, 1999, 2000a, 2001a, 2002a) and the American Iron and Steel Institute (AISI), *Annual Statistical Report* (AISI 2001, 2002, 2003, 2004). Scrap steel and imported pig iron consumption data for 1990 through 2003 were obtained from *Annual Statistical Reports* (AISI 1995, 2001, 2002, 2003, 2004) (see Table 4-6). Crude steel production, as well as pig iron use for purposes other than steel production, was also obtained from *Annual Statistical Reports* (AISI 1996, 2001, 2002, 2004). Carbon content percentages for pig iron and crude steel and the CO_2 emission factor for carbon anode emissions from steel production were obtained from *IPCC Good Practice Guidance and Uncertainty Management* (IPCC 2000). Aluminum production data for 1990 through 2003 were obtained from *Mineral Industry Surveys: Aluminum Annual Report* (USGS 1995b, 1998, 2000b, 2001b, 2002b, 2003, 2004a). Annual consumption of iron ore used in sinter production for 1990 through 2003 were obtained from the USGS Iron Ore yearbook (USGS 1994, 1995c, 1996, 1997b, 1998b, 1999b, 2000c, 2001c, 2002c, 2004b). The CO_2 emission factor for carbon anode emissions from aluminum production was taken from the *Revised 1996 IPCC Guidelines* (IPCC/UNEP/OECD/IEA 1997). Estimates for the composition of carbon anodes used during steel and aluminum production were obtained from *Energy and Environmental Profile of the U.S. Aluminum Industry* (DOE 1997).

Table 4-6: Production and Consumption Data for the Calculation of CO_2 and CH_4 Emissions from Iron and Steel Production (Thousand Metric Tons)

Gas/Activity Data	1990		1997	1998	1999	2000	2001	2002	2003
CO_2									
Coal Consumption at Coke Plants	35,289		27,400	25,573	25,499	26,253	23,655	21,460	21,997

Coke Consumption for Pig Iron	24,946	22,100	19,800	18,700	19,215	17,129	15,850	15,379
Domestic Pig Iron Production for Steel	49,061	48,676	47,470	45,677	47,399	41,740	39,600	40,487
Basic Oxygen Furnace Steel Production	56,227	55,386	54,146	52,364	53,964	47,359	45,463	45,873
Electric Arc Furnace Steel Production	33,517	43,098	44,513	45,063	47,859	42,743	46,124	47,803
CH_4								
Coke Production	25,054	20,063	18,181	18,240	18,877	17,190	15,220	15,579
Iron Ore Consumption for Sinter	12,239	11,426	10,791	11,072	10,784	9,234	9,018	8,984
Domestic Pig Iron Production for Steel	49,061	48,676	47,470	45,677	47,399	41,740	39,600	40,487

Uncertainty

The time series data for production of coal coke, sinter, pig iron, steel, and aluminum and import and export data upon which the calculations are based are considered to be consistent for the entire time series. The estimates of CO_2 emissions from the production and utilization of coke are based on energy consumption data, average carbon contents, and the fraction of carbon oxidized. These data and factors produce a relatively accurate estimate of CO_2 emissions. However, there are uncertainties associated with each of these factors. For example, carbon oxidation factors may vary depending on inefficiencies in the combustion process, where varying degrees of ash or soot can remain unoxidized.

Simplifying assumptions were made concerning the composition of carbon anodes (80 percent petroleum coke and 20 percent coal tar). For example, within the aluminum industry, the coal tar pitch content of anodes can vary from 15 percent in prebaked anodes to 24 to 28 percent in Soderberg anode pastes (DOE 1997). An average value was assumed and applied to all carbon anodes utilized during aluminum and steel production. The assumption is also made that all coal tar used during anode production originates as a by-product of the domestic coking process. Similarly, it was assumed that all pig iron and crude steel have carbon contents of 4 percent and 0.4 percent, respectively. The carbon content of pig iron can vary between 3 and 5 percent, while crude steel can have a carbon content of up to 2 percent, although it is typically less than 1 percent (IPCC 2000).

There is uncertainty in the most accurate CO_2 emission factor for carbon anode consumption in aluminum production. Emissions vary depending on the specific technology used by each plant (Prebake or Soderberg). The *Revised 1996 IPCC Guidelines* (IPCC/UNEP/OECD/IEA 1997) provide CO_2 emission factors for each technology type. Consistent with the assumptions used in the Aluminum Production source, it was assumed that production was split 80 percent prebake and 20 percent Soderberg for the whole time series. Similarly, the carbon anode emission factor for steel production can vary between 3.7 and 5.5 kg CO_2/ton steel (IPCC 2000). For this analysis, the upper bound value was used.

For the purposes of the CH_4 calculation it is assumed that none of the CH_4 is captured in stacks or vents and that all of the CH_4 escapes as fugitive emissions. Additionally, the CO_2 emissions calculation is not corrected by subtracting the carbon content of the CH_4, which means there may be a slight double counting of carbon as both CO_2 and CH_4.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-7. Iron and Steel CO_2 emissions were estimated to be between 32.0 and 76.4 Tg CO_2 Eq. at the 95 percent confidence level (or in 19 out of 20 Monte Carlo Stochastic Simulations). This indicates a range of approximately 41 percent below and 42 percent above the emission estimate of 53.8 Tg CO_2 Eq. Iron and Steel CH_4 emissions were estimated to be between 0.9 Tg CO_2 Eq. and 1.1 Tg CO_2 Eq. at the 95 percent confidence level (or in 19 out of 20 Monte Carlo Stochastic Simulations). This indicates a range of approximately 11 percent below and 11 percent above the emission estimate of 1.0 Tg CO_2 Eq.

Table 4-7: Tier 2 Quantitative Uncertainty Estimates for CO_2 and CH_4 Emissions from Iron and Steel Production (Tg. CO_2 Eq. and Percent)

Source	**Gas**	**2003 Emission Estimate**	**Uncertainty Range Relative to Emission Estimate**[a]	
		(Tg CO_2 Eq.)	**(Tg CO_2 Eq.)**	**(%)**

			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Iron and Steel	CO_2	53.8	32.0	76.4	-41%	+42%
Iron and Steel	CH_4	1.0	0.9	1.1	-11%	+11%

[a] Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

Recalculations Discussion

Estimates of CO_2 from iron and steel production increased due to revised production data found in American Iron and Steel Institute's *2003 Annual Statistical Report* (AISI 2004) and EIA's *2003 Quarterly Coal Report* (EIA 2004). These changes resulted in an average increase of 0.2 Tg CO_2 Eq. (0.5 percent) in CO_2 emissions from iron and steel production for 2001 and 2002.

Estimates of CH_4 2002 were revised due to revised sinter production data provided by the U.S. Geological Survey's *Iron and Steel Report 2003* (USGE 2004b). This change resulted in an increase of less than 0.1 Tg CO_2 Eq. (0.8 percent) in CH_4 emissions from iron and steel production for 2002.

4.2. Cement Manufacture (IPCC Source Category 2A1)

Cement manufacture is an energy and raw material intensive process that results in the generation of CO_2 from both the energy consumed in making the cement and the chemical process itself.[1] Cement production has accounted for about 2.4 percent of total global industrial and energy-related CO_2 emissions, and the United States is the world's third largest cement producer (IPCC 1997, USGS 2003). Cement is manufactured in nearly 40 states. Carbon dioxide emitted from the chemical process of cement production represents one of the largest sources of industrial CO_2 emissions in the United States.

During the cement production process, calcium carbonate ($CaCO_3$) is heated in a cement kiln at a temperature of about 1,300^{o}C (2,400^{o}F) to form lime (i.e., calcium oxide or CaO) and CO_2. This process is known as calcination or calcining. Next, the lime is combined with silica-containing materials to produce clinker (an intermediate product), with the earlier by-product CO_2 being released to the atmosphere. The clinker is then allowed to cool, mixed with a small amount of gypsum, and used to make portland cement. The production of masonry cement from portland cement requires additional lime and, thus, results in additional CO_2 emissions. However, this additional lime is already accounted for in the Lime Manufacture source category in this chapter; therefore, the additional emissions from making masonry cement from clinker are not counted in this source category's total. They are presented here for informational purposes only.

In 2003, U.S. clinker production—including Puerto Rico—totaled 83,214 thousand metric tons (Van Oss 2004). The resulting emissions of CO_2 from 2003 cement production were estimated to be 43.0 Tg CO_2 Eq. (43,030 Gg) (see Table 4-8). Emissions from masonry production from clinker raw material are accounted for under Lime Manufacture.

Table 4-8: CO_2 Emissions from Cement Production (Tg CO_2 Eq. and Gg)*

Year	Tg CO_2 Eq.	Gg
1990	33.3	33,278
1997	38.3	38,323
1998	39.2	39,218
1999	40.0	39,991

[1] The CO_2 emissions related to the consumption of energy for cement manufacture are accounted for under CO_2 from Fossil Fuel Combustion in the Energy chapter.

2000	41.2	41,190
2001	41.4	41,357
2002	42.9	42,898
2003	43.0	43,030

* Totals exclude CO_2 emissions from making masonry cement from clinker, which are accounted for under Lime Manufacture.

After falling in 1991 by two percent from 1990 levels, cement production emissions have grown every year since. Overall, from 1990 to 2003, emissions increased by 29 percent. Cement is a critical component of the construction industry; therefore, the availability of public construction funding, as well as overall economic growth, have had considerable influence on cement production.

Methodology

Carbon dioxide emissions from cement manufacture are created by the chemical reaction of carbon-containing minerals (i.e., calcining limestone). While in the kiln, limestone is broken down into CO_2 and lime with the CO_2 released to the atmosphere. The quantity of the CO_2 emitted during cement production is directly proportional to the lime content of the clinker. During calcination, each mole of $CaCO_3$ (i.e., limestone) heated in the clinker kiln forms one mole of lime (CaO) and one mole of CO_2:

$$CaCO_3 + \text{heat} \rightarrow CaO + CO_2$$

Carbon dioxide emissions were estimated by applying an emission factor, in tons of CO_2 released per ton of clinker produced, to the total amount of clinker produced. The emission factor used in this analysis is the product of the average lime fraction for clinker of 64.6 percent (IPCC 2000) and a constant reflecting the mass of CO_2 released per unit of lime. This calculation yields an emission factor of 0.507 tons of CO_2 per ton of clinker produced, which was determined as follows:

$$EF_{\text{Clinker}} = 0.646\ \text{CaO} \times \left[\frac{44.01\ \text{g/mole}\ CO_2}{56.08\ \text{g/mole}\ \text{CaO}}\right] = 0.507\ \text{tons}\ CO_2/\text{ton clinker}$$

During clinker production, some of the clinker precursor materials remain in the kiln as non-calcinated, partially calcinated, or fully calcinated cement kiln dust (CKD). The emissions attributable to the calcinated portion of the CKD are not accounted for by the clinker emission factor. The IPCC recommends that these additional CKD CO_2 emissions should be estimated as two percent of the CO_2 emissions calculated from clinker production. Total cement production emissions were calculated by adding the emissions from clinker production to the emissions assigned to CKD (IPCC 2000).

Masonry cement requires additional lime over and above the lime used in clinker production. In particular, non-plasticizer additives such as lime, slag, and shale are added to the cement, increasing its weight by approximately five percent. Lime accounts for approximately 60 percent of this added weight. Thus, the additional lime is equivalent to roughly 2.86 percent of the starting amount of the product, since:

$$0.6 \times 0.05/(1 + 0.05) = 2.86\%$$

An emission factor for this added lime can then be calculated by multiplying this 2.86 percent by the molecular weight ratio of CO_2 to CaO (0.785) to yield 0.0224 metric tons of additional CO_2 emitted for every metric ton of masonry cement produced.

As previously mentioned, the CO_2 emissions from the additional lime added during masonry cement production are accounted for in the section on CO_2 emissions from Lime Manufacture. Thus, the activity data for masonry cement production are shown in this chapter for informational purposes only, and are not included in the cement emission totals.

The 1990 through 2003 activity data for clinker and masonry cement production (see Table 4-9) was obtained through a personal communication with Hendrick Van Oss (Van Oss 2004) of the USGS and through the USGS *Mineral Yearbook: Cement* (USGS 1992 through 2003). Data for 2003 masonry cement production were unavailable and were assumed to equal 2002 data. The data were compiled by USGS through questionnaires sent to domestic clinker and cement manufacturing plants.

Table 4-9: Cement Production (Gg)

Year	Clinker	Masonry
1990	64,355	3,209
1991	62,918	2,856
1992	63,415	3,093
1993	66,957	2,975
1994	69,786	3,283
1995	71,257	3,603
1996	71,706	3,469
1997	74,112	3,634
1998	75,842	3,989
1999	77,337	4,375
2000	79,656	4,332
2001	79,979	4,450
2002	82,959	4,449
2003	83,214	4,449

Uncertainty

The uncertainties contained in these estimates are primarily due to uncertainties in the lime content of clinker and in the percentage of CKD recycled inside the clinker kiln. There is also an uncertainty in the amount of lime added to masonry cement, but it is accounted for under the Lime Manufacture source category. The lime content of clinker varies from 64 to 66 percent. CKD loss can range from 1.5 to eight percent depending upon plant specifications. Additionally, some amount of CO_2 is reabsorbed when the cement is used for construction. As cement reacts with water, alkaline substances such as calcium hydroxide are formed. During this curing process, these compounds may react with CO_2 in the atmosphere to create calcium carbonate. This reaction only occurs in roughly the outer 0.2 inches of surface area. Because the amount of CO_2 reabsorbed is thought to be minimal, it was not estimated.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-10. Cement Manufacture CO_2 emissions were estimated to be between 39.7 and 46.3 Tg CO_2 Eq. at the 95 percent confidence level (or in 19 out of 20 Monte Carlo Stochastic Simulations). This indicates a range of approximately 8 percent below and 8 percent above the emission estimate of 43.0 Tg CO_2 Eq.

Table 4-10: Tier 2 Quantitative Uncertainty Estimates for CO_2 Emissions from Cement Manufacture (Tg CO_2 Eq. and Percent)

Source	Gas	2003 Emission Estimate (Tg CO_2 Eq.)	Uncertainty Range Relative to Emission Estimate[a] (Tg CO_2 Eq.)		Uncertainty Range Relative to Emission Estimate[a] (%)	
			Lower Bound	**Upper Bound**	**Lower Bound**	**Upper Bound**
Cement Manufacture	CO_2	43.0	39.7	46.3	-8%	+8%

[a] Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

QA/QC and Verification

Based on the results of the Tier 2 uncertainty analysis conducted on the cement emissions estimate for the 2004 U.S. GHG Inventory, the United States decided to conduct Tier 2 QA procedures on two elements of the cement emissions estimate for the current inventory submission: the CaO content of clinker and emissions from production of CKD. The United States currently uses the IPCC default values for these input values and the current investigation seeks to determine whether these default values are reflective of U.S. circumstances. We are currently in the process of conducting a form of expert elicitation on these values. Preliminary results suggest that the default values seem appropriate for the U.S. cement industry however there may be small differences. We are currently investigating any differences and will include any results in future inventories, if appropriate.

4.3. Ammonia Manufacture and Urea Application (IPCC Source Category 2B1)

Emissions of CO_2 occur during the production of synthetic ammonia, primarily through the use of natural gas as a feedstock. One ammonia production plant located in Kansas is producing ammonia from petroleum coke feedstock. The natural gas-based, naphtha-based, and petroleum coke-based processes produce CO_2 and hydrogen (H_2), the latter of which is used in the production of ammonia. In some plants the CO_2 produced is captured and used to produce urea. The brine electrolysis process for production of ammonia does not lead to CO_2 emissions.

There are five principal process steps in synthetic ammonia production from natural gas feedstock. The primary reforming step converts CH_4 to CO_2, carbon monoxide (CO), and H_2 in the presence of a catalyst. Only 30 to 40 percent of the CH_4 feedstock to the primary reformer is converted to CO and CO_2. The secondary reforming step converts the remaining CH_4 feedstock to CO and CO_2. The CO in the process gas from the secondary reforming step (representing approximately 15 percent of the process gas) is converted to CO_2 in the presence of a catalyst, water, and air in the shift conversion step. Carbon dioxide is removed from the process gas by the shift conversion process, and the hydrogen gas is combined with the nitrogen (N_2) gas in the process gas during the ammonia synthesis step to produce ammonia. The CO_2 is included in a waste gas stream with other process impurities and is absorbed by a scrubber solution. In regenerating the scrubber solution, CO_2 is released.

The conversion process for conventional steam reforming of CH_4, including primary and secondary reforming and the shift conversion processes, is approximately as follows:

$$0.88\ CH_4 + 1.26\ \text{Air} + 1.24\ H_2O \xrightarrow{\text{(catalyst)}} 0.88\ CO_2 + N_2 + 3\ H_2$$

$$N_2 + 3\ H_2 \rightarrow 2\ NH_3$$

To produce synthetic ammonia from petroleum coke, the petroleum coke is gasified and converted to CO_2 and H_2. These gases are separated, and the H_2 is used as a feedstock to the ammonia production process, where it is reacted with N_2 to form ammonia.

Not all of the CO_2 produced in the production of ammonia is emitted directly to the atmosphere. Both ammonia and carbon dioxide are used as raw materials in the production of urea [$CO(NH_2)_2$], which is another type of nitrogenous fertilizer that contains carbon as well as nitrogen. The chemical reaction that produces urea is:

$$2\ NH_3 + CO_2 \rightarrow\ NH_2COONH_4 \rightarrow CO(NH_2)_2 + H_2O$$

The carbon in the urea that is produced and assumed to be subsequently applied to agricultural land as a nitrogenous fertilizer is ultimately released into the environment as CO_2; therefore, the CO_2 produced by ammonia production and subsequently used in the production of urea does not change overall CO_2 emissions. However, the CO_2 emissions are allocated to the ammonia and urea production processes in accordance to the amount of ammonia and urea produced.

Net emissions of CO_2 from ammonia manufacture in 2003 were 9.1 Tg CO_2 Eq. (9,097 Gg), and are summarized in Table 4-11 and Table 4-12. Emissions of CO_2 from urea application in 2003 totaled 6.5 Tg CO_2 Eq. (6,463Gg), and are summarized in Table 4-11 and Table 4-12.

Table 4-11: CO_2 Emissions from Ammonia Manufacture and Urea Application (Tg CO_2 Eq.)

Source	1990		1997	1998	1999	2000	2001	2002	2003

Ammonia Manufacture	12.6		14.0	14.2	12.9	12.1	9.3	10.6	9.1
Urea Application	6.8		6.6	7.7	7.7	7.5	7.4	8.0	6.5
Total	**19.3**		**20.7**	**21.9**	**20.6**	**19.6**	**16.7**	**18.6**	**15.6**

Table 4-12: CO_2 Emissions from Ammonia Manufacture and Urea Application (Gg)

Source	**1990**		**1997**	**1998**	**1999**	**2000**	**2001**	**2002**	**2003**
Ammonia Manufacture	12,553		14,028	14,215	12,948	12,128	9,321	10,561	9,097
Urea Application	6,753		6,622	7,719	7,667	7,488	7,398	8,010	6,463

Methodology

The calculation methodology for non-combustion CO_2 emissions from production of nitrogenous fertilizers from natural gas feedstock is based on a CO_2 emission factor published by the European Fertilizer Manufacturers Association (EFMA). The CO_2 emission factor (1.2 metric tons CO_2/metric ton NH_3) is applied to the percent of total annual domestic ammonia production from natural gas feedstock. Emissions of CO_2 from ammonia production are then adjusted to account for the use of some of the CO_2 produced from ammonia production as a raw material in the production of urea. For each ton of urea produced, 8.8 of every 12 tons of CO_2 are consumed and 6.8 of every 12 tons of ammonia are consumed. The CO_2 emissions reported for ammonia production are therefore reduced by a factor of 0.73 multiplied by total annual domestic urea production, and that amount of CO_2 emissions is allocated to urea fertilizer application. Total CO_2 emissions resulting from nitrogenous fertilizer production do not change as a result of this calculation, but some of the CO_2 emissions are attributed to ammonia production and some of the CO_2 emissions are attributed to urea application.

The calculation of the total non-combustion CO_2 emissions from nitrogenous fertilizers accounts for CO_2 emissions from the application of imported and domestically produced urea. For each ton of imported urea applied, 0.73 tons of CO_2 are emitted to the atmosphere. The amount of imported urea applied is calculated based on the net of urea imports and exports.

All ammonia production and subsequent urea production are assumed to be from the same process—conventional catalytic reforming of natural gas feedstock, with the exception of ammonia production from petroleum coke feedstock at one plant located in Kansas. The CO_2 emission factor for production of ammonia from petroleum coke is based on plant specific data, wherein all carbon contained in the petroleum coke feedstock that is not used for urea production is assumed to be emitted to the atmosphere as CO_2 (Bark 2004). Ammonia and urea are assumed to be manufactured in the same manufacturing complex, as both the raw materials needed for urea production are produced by the ammonia production process. The CO_2 emission factor (3.57 metric tons CO_2/metric ton NH_3) is applied to the percent of total annual domestic ammonia production from petroleum coke feedstock.

The emission factor of 1.2 metric ton CO_2/metric ton NH_3 for production of ammonia from natural gas feedstock was taken from the European Fertilizer Manufacturers Association Best Available Techniques publication, *Production of Ammonia* (EFMA 1995). The EFMA reported an emission factor range of 1.15 to 1.30 metric ton CO_2/metric ton NH_3, with 1.2 metric ton CO_2/metric ton NH_3 as a typical value. The EFMA reference also indicates that more than 99 percent of the CH_4 feedstock to the catalytic reforming process is ultimately converted to CO_2. The emission factor of 3.57 metric ton CO_2/metric ton NH_3 for production of ammonia from petroleum coke feedstock was developed from plant-specific ammonia production data and petroleum coke feedstock utilization data for the ammonia plant located in Kansas (Bark 2004). Ammonia and urea production data (see Table 4-13 and Table 4-14, respectively) were obtained from the Census Bureau of the U.S. Department of Commerce (U.S. Census Bureau 1991 through 2004) as reported in *Current Industrial Reports Fertilizer Materials and Related Products* annual and quarterly reports. Import and export data for 2003 were unavailable and were assumed to equal 2002 data (see Table 4-15). These data were obtained from the U.S. Census Bureau *Current Industrial Reports Fertilizer Materials and Related Products* annual reports (U.S. Census Bureau) for 1997 through 2002, The Fertilizer Institute (TFI 2002) for 1993 through 1996, and the United States International Trade Commission Interactive Tariff and Trade DataWeb (U.S. ITC 2002) for 1990 through 1992.

Table 4-13: Ammonia Production (Gg)

Year	Gg
1990	15,425
1991	15,576
1992	16,261
1993	15,599
1994	16,211
1995	15,788
1996	16,260
1997	16,231
1998	16,761
1999	15,728
2000	14,342
2001	11,092
2002	12,577
2003	10,468

Table 4-14: Urea Production (Gg)

Year	Gg
1990	8,124
1991	7,373
1992	8,142
1993	7,557
1994	7,584
1995	7,363
1996	7,755
1997	7,430
1998	8,042
1999	8,080
2000	6,969
2001	6,080
2002	7,038
2003	5,783

Table 4-15: Urea Net Imports (Gg)

Year	Gg
1990	1,086
1991	648
1992	656
1993	2,305
1994	2,249
1995	2,055
1996	1,051
1997	1,600
1998	2,483
1999	2,374
2000	3,241
2001	4,008
2002	3,884
2003	3,030

Uncertainty

The uncertainties contained in these estimates are primarily due to how accurately the emission factor used represents an average across all ammonia plants using natural gas feedstock. The EFMA reported an emission factor range of 1.15 to 1.30 ton CO_2/ton NH_3, with 1.2 ton CO_2/ton NH_3 reported as a typical value. The actual emission factor depends upon the amount of air used in the ammonia production process, with 1.15 ton CO_2/ton NH_3 being the approximate stoichiometric minimum that is achievable for the conventional reforming process. By using natural gas consumption data for each ammonia plant, more accurate estimates of CO_2 emissions from ammonia production could be calculated. However, these consumption data are often considered confidential. Also, natural gas is consumed at ammonia plants both as a feedstock to the reforming process and for generating process heat and steam. Natural gas consumption data, if available, would need to be divided into feedstock use (non-energy) and process heat and steam (fuel) use, as CO_2 emissions from fuel use and non-energy use are calculated separately.[2]

Natural gas feedstock consumption data for the U.S. ammonia industry as a whole is available from the Energy Information Administration (EIA) *Manufacturers Energy Consumption Survey* (MECS) for the years 1985, 1988, 1991, 1994 and 1998 (EIA 1994; EIA 1998). These feedstock consumption data collectively correspond to an effective average emission factor of 1.0 ton CO_2/ton NH_3, which appears to be below the stoichiometric minimum that is achievable for the conventional steam reforming process. The EIA data for natural gas consumption for the years 1994 and 1998 correspond more closely to the CO_2 emissions calculated using the EFMA emission factor than do data for previous years. The 1994 and 1998 data alone yield an effective emission factor of 1.1 ton CO_2/ton NH_3, corresponding to CO_2 emissions estimates that are approximately 1.5 Tg CO_2 Eq. below the estimates calculated using the EFMA emission factor of 1.2 ton CO_2/ton NH_3. Natural gas feedstock consumption data are not available from EIA for other years, and data for 1991 and previous years may underestimate feedstock natural gas consumption, and therefore the EFMA emission factor was used to estimate CO_2 emissions from ammonia production, rather than EIA data.

All ammonia production and subsequent urea production was assumed to be from the same process—conventional catalytic reforming of natural gas feedstock, with the exception of one ammonia production plant located in Kansas that is manufacturing ammonia from petroleum coke feedstock. Research indicates that there is only one U.S. plant that manufactures ammonia from petroleum coke. CO_2 emissions from this plant are explicitly accounted for in the Inventory estimates. No data for ammonia plants using naphtha or other feedstocks other than natural gas have been identified. Therefore, all other CO_2 emissions from ammonia plants are calculated using the emission factor for natural gas feedstock. However, actual emissions may differ because processes other than catalytic steam reformation and feedstocks other than natural gas may have been used for ammonia production. Urea is also used for other purposes than as a nitrogenous fertilizer. It was assumed that 100 percent of the urea production and net imports are used as fertilizer or in otherwise emissive uses. It is also assumed that ammonia and urea are produced at collocated plants from the same natural gas raw material.

Such recovery may or may not affect the overall estimate of CO_2 emissions from that sector depending upon the end use to which the recovered CO_2 is applied. For example, research has identified one ammonia production plant that is recovering byproduct CO_2 for use in EOR. Such CO_2 would be assumed to remain sequestered [see the section of

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[2] It appears that the IPCC emission factor for ammonia production of 1.5 ton CO_2 per ton ammonia may include both CO_2 emissions from the natural gas feedstock to the process and some CO_2 emissions from the natural gas used to generate process heat and steam for the process. Table 2-5, Ammonia Production Emission Factors, in Volume 3 of the Revised 1996 IPCC Guidelines for National Greenhouse Gas Inventories Reference Manual (IPCC 1997) includes two emission factors, one reported for Norway and one reported for Canada. The footnotes to the table indicate that the factor for Norway does not include natural gas used as fuel but that it is unclear whether the factor for Canada includes natural gas used as fuel. However, the factors for Norway and Canada are nearly identical (1.5 and 1.6 tons CO_2 per ton ammonia, respectively) and it is likely that if one value does not include fuel use, the other value also does not. For the conventional steam reforming process, however, the EFMA reports an emission factor range for feedstock CO_2 of 1.15 to 1.30 ton per ton (with a typical value of 1.2 ton per ton) and an emission factor for fuel CO_2 of 0.5 tons per ton. This corresponds to a total CO_2 emission factor for the ammonia production process, including both feedstock CO_2 and process heat CO_2, of 1.7 ton per ton, which is closer to the emission factors reported in the IPCC 1996 Reference Guidelines than to the feedstock-only CO_2 emission factor of 1.2 ton CO_2 per ton ammonia reported by the EFMA. Because it appears that the emission factors cited in the IPCC Guidelines may actually include natural gas used as fuel, we use the 1.2 tons/ton emission factor developed by the EFMA.

this chapter on Carbon Dioxide Consumption] however, time series data for the amount of CO_2 recovered from this plant is not available and therefore all of the CO_2 produced by this plant is assumed to be emitted to the atmosphere and allocated to Ammonia Manufacture. Further research is required to determine whether byproduct CO_2 is being recovered from other ammonia production plants for application to end uses that are not accounted for elsewhere.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-16. Ammonia CO_2 emissions were estimated to be between 7.7 and 10.4 Tg CO_2 Eq. at the 95 percent confidence level (or in 19 out of 20 Monte Carlo Stochastic Simulations). This indicates a range of approximately 15 percent below and 15 percent above the emission estimate of 9.1 Tg CO_2 Eq. Urea CO_2 emissions were estimated to be between 6.0 and 7.0 Tg CO_2 Eq. at the 95 percent confidence level (or in 19 out of 20 Monte Carlo Stochastic Simulations). This indicates a range of approximately 8 percent below and 8 percent above the emission estimate of 6.5 Tg CO_2 Eq.

Table 4-16: Tier 2 Quantitative Uncertainty Estimates for CO_2 Emissions from Ammonia Manufacture and Urea Application (Tg CO_2 Eq. and Percent)

Source	Gas	2003 Emission Estimate (Tg CO_2 Eq.)	Uncertainty Range Relative to Emission Estimate[a] (Tg CO_2 Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Ammonia	CO_2	9.1	7.7	10.4	-15%	+15%
Urea	CO_2	6.5	6.0	7.0	-8%	+8%

[a] Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

Recalculations Discussion

Estimates of CO_2 emissions from ammonia manufacture for the years 2000, 2001, and 2002 were updated to reflect revisions made to the methodology to include ammonia manufactured from petroleum coke. The plant, located in Kansas, began ammonia production in 2000. This change resulted in an average annual increase in CO_2 emissions from ammonia manufacture of 0.5 Tg CO_2 Eq. (2.7 percent) for the years 2000 through 2002.

Planned Improvements

The United States recognizes that the Tier 2 methodology is preferred for estimating CO_2 emissions from ammonia manufacture. Historically, efforts have been made to acquire feedstock data for this source category however the relevant data were not available. In addition to some of the future work noted in the Uncertainty section, additional planned improvements for this source category include developing a plan to determine the feasibility of acquiring the relevant data for the Tier 2 assessment. If successful, the results will be included in future inventory submissions.

4.4. Lime Manufacture (IPCC Source Category 2A2)

Lime is an important manufactured product with many industrial, chemical, and environmental applications. Its major uses are in steel making, flue gas desulfurization (FGD) systems at coal-fired electric power plants, construction, and water purification. Lime has historically ranked fifth in total production of all chemicals in the United States. For U.S. operations, the term "lime" actually refers to a variety of chemical compounds. These include calcium oxide (CaO), or high-calcium quicklime; calcium hydroxide ($Ca(OH)_2$), or hydrated lime; dolomitic quicklime ([CaO•MgO]); and dolomitic hydrate ([$Ca(OH)_2$•MgO] or [$Ca(OH)_2$•$Mg(OH)_2$]).

Lime production involves three main processes: stone preparation, calcination, and hydration. Carbon dioxide is generated during the calcination stage, when limestone—mostly calcium carbonate ($CaCO_3$)—is roasted at high temperatures in a kiln to produce CaO and CO_2. The CO_2 is given off as a gas and is normally emitted to the atmosphere. Some of the CO_2 generated during the production process, however, is recovered at some facilities for use in sugar refining and precipitated calcium carbonate (PCC)[3] production. It is also important to note that, for certain applications, lime reabsorbs CO_2 during use (see Uncertainty, below).

Lime production in the United States—including Puerto Rico—was reported to be 19,164 thousand metric tons in 2003 (USGS 2004). This resulted in estimated CO_2 emissions of 13.0 Tg CO_2 Eq. (or 12,983 Gg) (see Table 4-17 and Table 4-18).

Table 4-17: Net CO_2 Emissions from Lime Manufacture (Tg CO_2 Eq.)

Year	Tg CO_2 Eq.
1990	11.2
1997	13.7
1998	13.9
1999	13.5
2000	13.3
2001	12.8
2002	12.3
2003	13.0

Table 4-18: CO_2 Emissions from Lime Manufacture (Gg)

Year	Potential	Recovered*	Net Emissions
1990	11,730	(493)	11,238
1997	14,649	(964)	13,685
1998	14,975	(1,061)	13,914
1999	14,655	(1,188)	13,466
2000	14,548	(1,233)	13,315
2001	13,941	(1,118)	12,823
2002	13,355	(1,051)	12,304
2003	14,132	(1,149)	12,983

* For sugar refining and precipitated calcium carbonate production.
Note: Totals may not sum due to independent rounding.

At the turn of the 20th Century, over 80 percent of lime consumed in the United States went for construction uses. The contemporary quicklime market is distributed across four end-use categories as follows: metallurgical uses, 35 percent; environmental uses, 28 percent; chemical and industrial uses, 23 percent, construction uses, 13 percent; and refractory dolomite, one percent. In the construction sector, hydrated lime is still used to improve durability in plaster, stucco, and mortars. The use of hydrated lime for traditional building increased by nearly seven percent in 2003 (USGS 2004).

Lime production in 2003 increased by nearly seven percent from 2002, the first increase in production in five years. Overall, from 1990 to 2003, lime production has increased by 17 percent. The increase in production is attributed in part to growth in demand for environmental applications, especially flue gas desulfurization technologies. In 1993, EPA completed regulations under the Clean Air Act capping sulfur dioxide (SO_2) emissions from electric utilities. Lime scrubbers' high efficiencies and increasing affordability have allowed the flue gas desulfurization end-use to expand significantly over the years. Phase II of the Clean Air Act Amendments, which went into effect on January 1, 2000, remains the driving force behind the growth in the flue gas desulfurization market (USGS 2003).

[3] Precipitated calcium carbonate is a specialty filler used in premium-quality coated and uncoated papers.

Methodology

During the calcination stage of lime manufacture, CO_2 is given off as a gas and normally exits the system with the stack gas. To calculate emissions, the amounts of high-calcium and dolomitic lime produced were multiplied by their respective emission factors. The emission factor is the product of a constant reflecting the mass of CO_2 released per unit of lime and the average calcium plus magnesium oxide (CaO + MgO) content for lime (95 percent for both types of lime). The emission factors were calculated as follows:

For high-calcium lime: [(44.01 g/mole CO_2) ÷ (56.08 g/mole CaO)] × (0.95 CaO/lime) = 0.75 g CO_2/g lime

For dolomitic lime: [(88.02 g/mole CO_2) ÷ (96.39 g/mole CaO)] × (0.95 CaO/lime) = 0.87 g CO_2/g lime

Production is adjusted to remove the mass of chemically combined water found in hydrated lime, using the midpoint of default ranges provided by the *IPCC Good Practice Guidance* (IPCC 2000). These factors set the chemically combined water content to 27 percent for high-calcium hydrated lime, and 24 percent for dolomitic hydrated lime.

Lime production in the United States was 19,164 thousand metric tons in 2003 (USGS 2004), resulting in potential CO_2 emissions of 14.1 Tg CO_2 Eq. Some of the CO_2 generated during the production process, however, was recovered for use in sugar refining and precipitated calcium carbonate (PCC) production. Combined lime manufacture by these producers was 1,926 thousand metric tons in 2003. It was assumed that approximately 80 percent of the CO_2 involved in sugar refining and PCC was recovered, resulting in actual CO_2 emissions of 13.0 Tg CO_2 Eq.

The activity data for lime manufacture and lime consumption by sugar refining and PCC production for 1990 through 2003 (see Table 4-19) were obtained from USGS (1992 through 2004). Hydrated lime production is reported separately in Table 4-20. The CaO and CaO•MgO contents of lime were obtained from the *IPCC Good Practice Guidance* (IPCC 2000). Since data for the individual lime types (high calcium and dolomitic) was not provided prior to 1997, total lime production for 1990 through 1996 was calculated according to the three year distribution from 1997 to 1999. For sugar refining and PCC, it was assumed that 100 percent of lime manufacture and consumption was high-calcium, based on communication with the National Lime Association (Males 2003).

Table 4-19: Lime Production and Lime Use for Sugar Refining and PCC (Gg)

Year	High-Calcium Production[a]	Dolomitic Production[a,b]	Use for Sugar Refining and PCC
1990	12,947	2,895	826
1991	12,840	2,838	964
1992	13,307	2,925	1,023
1993	13,741	3,024	1,279
1994	14,274	3,116	1,374
1995	15,193	3,305	1,503
1996	15,856	3,434	1,429
1997	16,120	3,552	1,616
1998	16,750	3,423	1,779
1999	16,110	3,598	1,992
2000	15,850	3,621	2,067
2001	15,630	3,227	1,874
2002	14,900	3,051	1,762
2003	16,040	3,124	1,926

[a] Includes hydrated lime.
[b] Includes dead-burned dolomite.

Table 4-20: Hydrated Lime Production (Gg)

Year	High-Calcium Hydrate	Dolomitic Hydrate
1990	1,781	319

1991	1,841	329
1992	1,892	338
1993	1,908	342
1994	1,942	348
1995	2,027	363
1996	1,858	332
1997	1,820	352
1998	1,950	383
1999	2,010	298
2000	1,550	421
2001	2,030	447
2002	1,500	431
2003	2,140	464

Uncertainty

The uncertainties contained in these estimates can be attributed to slight differences in the chemical composition of these products. Although the methodology accounts for various formulations of lime, it does not account for the trace impurities found in lime, such as iron oxide, alumina, and silica. Due to differences in the limestone used as a raw material, a rigid specification of lime material is impossible. As a result, few plants manufacture lime with exactly the same properties.

In addition, a portion of the CO_2 emitted during lime manufacture will actually be reabsorbed when the lime is consumed. As noted above, lime has many different chemical, industrial, environmental, and construction applications. In many processes, CO_2 reacts with the lime to create calcium carbonate (e.g., water softening). Carbon dioxide reabsorption rates vary, however, depending on the application. For example, 100 percent of the lime used to produce precipitated calcium carbonate reacts with CO_2; whereas most of the lime used in steel making reacts with impurities such as silica, sulfur, and aluminum compounds. A detailed accounting of lime use in the United States and further research into the associated processes are required to quantify the amount of CO_2 that is reabsorbed.[4]

In some cases, lime is generated from calcium carbonate by-products at pulp mills and water treatment plants.[5] The lime generated by these processes is not included in the USGS data for commercial lime consumption. In the pulping industry, mostly using the Kraft (sulfate) pulping process, lime is consumed in order to causticize a process liquor (green liquor) composed of sodium carbonate and sodium sulfide. The green liquor results from the dilution of the smelt created by combustion of the black liquor where biogenic carbon is present from the wood. Kraft mills recover the calcium carbonate “mud” after the causticizing operation and most sulfate mills recover the waste calcium carbonate after the causticizing operation and calcine it back into lime—thereby generating CO_2—for reuse in the pulping process. Although this re-generation of lime could be considered a lime manufacturing process, the CO_2 emitted during this process is mostly biogenic in origin, and therefore is not included in Inventory totals.

In the case of water treatment plants, lime is used in the softening process. Some large water treatment plants may recover their waste calcium carbonate and calcine it into quicklime for reuse in the softening process. Further

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[4] Representatives of the National Lime Association estimate that CO_2 reabsorption that occurs from the use of lime may offset as much as a quarter of the CO_2 emissions from calcination (Males 2003).

[5] Some carbide producers may also regenerate lime from their calcium hydroxide by-products, which does not result in emissions of CO_2. In making calcium carbide, quicklime is mixed with coke and heated in electric furnaces. The regeneration of lime in this process is done using a waste calcium hydroxide (hydrated lime) [$CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2$], not calcium carbonate [$CaCO_3$]. Thus, the calcium hydroxide is heated in the kiln to simply expel the water [$Ca(OH)_2$ + heat $\rightarrow CaO + H_2O$] and no CO_2 is released.

research is necessary to determine the degree to which lime recycling is practiced by water treatment plants in the United States.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-21. Lime CO_2 emissions were estimated to be between 12.0 and 14.1 Tg CO_2 Eq. at the 95 percent confidence level (or in 19 out of 20 Monte Carlo Stochastic Simulations). This indicates a range of approximately 8 percent below and 8 percent above the emission estimate of 13.0 Tg CO_2 Eq.

Table 4-21: Tier 2 Quantitative Uncertainty Estimates for CO_2 Emissions from Lime Manufacture (Tg CO_2 Eq. and Percent)

Source	**Gas**	**2003 Emission Estimate (Tg CO_2 Eq.)**	**Uncertainty Range Relative to Emission Estimate[a] (Tg CO_2 Eq.)**		**(%)**	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Lime Manufacture	CO_2	13.0	12.0	14.1	-8%	+8%

[a] Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

4.5. Limestone and Dolomite Use (IPCC Source Category 2A3)

Limestone ($CaCO_3$) and dolomite ($CaCO_3MgCO_3$)[6] are basic raw materials used by a wide variety of industries, including construction, agriculture, chemical, metallurgy, glass manufacture, and environmental pollution control. Limestone is widely distributed throughout the world in deposits of varying sizes and degrees of purity. Large deposits of limestone occur in nearly every state in the United States, and significant quantities are extracted for industrial applications. For some of these applications, limestone is sufficiently heated during the process to generate CO_2 as a by-product. Examples of such applications include limestone used as a flux or purifier in metallurgical furnaces, as a sorbent in flue gas desulfurization systems for utility and industrial plants, or as a raw material in glass manufacturing and magnesium production.

In 2003, approximately 8,074 thousand metric tons of limestone and 2,446 thousand metric tons of dolomite were consumed for these applications. Overall, usage of limestone and dolomite resulted in aggregate CO_2 emissions of 4.7 Tg CO_2 Eq. (4,720 Gg) (see Table 4-22 and Table 4-23). Emissions in 2003 decreased 20 percent from the previous year and have decreased 15 percent overall from 1990 through 2003.

Table 4-22: CO_2 Emissions from Limestone & Dolomite Use (Tg CO_2 Eq.)

Activity	**1990**		**1997**	**1998**	**1999**	**2000**	**2001**	**2002**	**2003**
Flux Stone	3.0		5.0	5.1	6.0	2.8	2.5	2.4	2.1
Glass Making	0.2		0.3	0.2	0	0.4	0.1	0.1	0.3
FGD	1.4		1.4	1.2	1.2	1.8	2.6	2.8	1.9
Magnesium Production	0.1		0.1	0.1	0.1	0.1	0.1	0.0	0.0
Other Miscellaneous Uses	0.8		0.4	0.9	0.7	0.9	0.5	0.7	0.4
Total	**5.5**		**7.2**	**7.4**	**8.1**	**6.0**	**5.7**	**5.9**	**4.7**

Notes: Totals may not sum due to independent rounding. Other miscellaneous uses include chemical stone, mine dusting or acid water treatment, acid neutralization, and sugar refining.

Table 4-23: CO_2 Emissions from Limestone & Dolomite Use (Gg)

Activity	**1990**		**1997**	**1998**	**1999**	**2000**	**2001**	**2002**	**2003**
Flux Stone	2,999		5,023	5,132	6,030	2,829	2,514	2,405	2,072

[6] Limestone and dolomite are collectively referred to as limestone by the industry, and intermediate varieties are seldom distinguished.

Limestone	2,554	3,963	4,297	4,265	1,810	1,640	1,330	904
Dolomite	446	1,060	835	1,765	1,020	874	1,075	1,168
Glass Making	217	319	157	0	368	113	61	337
Limestone	189	319	65	0	368	113	61	337
Dolomite	28	0	91	0	0	0	0	0
FGD	1,433	1,426	1,230	1,240	1,773	2,551	2,766	1,932
Magnesium Production	64	73	73	73	73	53	0	0
Other Miscellaneous Uses	819	401	858	713	915	501	652	380
Total	**5,533**	**7,242**	**7,449**	**8,057**	**5,959**	**5,733**	**5,885**	**4,720**

Notes: Totals may not sum due to independent rounding. Other miscellaneous uses include chemical stone, mine dusting or acid water treatment, acid neutralization, and sugar refining.

Methodology

Carbon dioxide emissions were calculated by multiplying the quantity of limestone or dolomite consumed by the average carbon content, approximately 12.0 percent for limestone and 13.2 percent for dolomite (based on stoichiometry). This assumes that all carbon is oxidized and released. This methodology was used for flux stone, glass manufacturing, flue gas desulfurization systems, chemical stone, mine dusting or acid water treatment, acid neutralization, and sugar refining and then converting to CO_2 using a molecular weight ratio.

Traditionally, the production of magnesium metal was the only other use of limestone and dolomite that produced CO_2 emissions. At the start of 2001, there were two magnesium production plants operating in the United States and they used different production methods. One plant produced magnesium metal using a dolomitic process that resulted in the release of CO_2 emissions, while the other plant produced magnesium from magnesium chloride using a CO_2-emissions-free process called electrolytic reduction. However, the plant utilizing the dolomitic process ceased its operations prior to the end of 2001, so beginning in 2002 there were no emissions from this particular sub-use.

Consumption data for 1990 through 2003 of limestone and dolomite used for flux stone, glass manufacturing, flue gas desulfurization systems, chemical stone, mine dusting or acid water treatment, acid neutralization, and sugar refining (see Table 4-24) were obtained from personal communication with Valentine Tepordei of the USGS regarding data in the *Minerals Yearbook: Crushed Stone Annual Report* (Tepordei 2002, 2003, 2004 and USGS 1993, 1995a, 1995b, 1996a, 1997a, 1998a, 1999a, 2000a, 2001a, 2002a, 2003a). The production capacity data for 1990 through 2003 of dolomitic magnesium metal (see Table 4-25) also came from the USGS (1995c, 1996b, 1997b, 1998b, 1999b, 2000b, 2001b, 2002b, 2003b, 2004). During 1990 and 1992, the USGS did not conduct a detailed survey of limestone and dolomite consumption by end-use. Consumption for 1990 was estimated by applying the 1991 percentages of total limestone and dolomite use constituted by the individual limestone and dolomite uses to 1990 total use. Similarly, the 1992 consumption figures were approximated by applying an average of the 1991 and 1993 percentages of total limestone and dolomite use constituted by the individual limestone and dolomite uses to the 1992 total.

Additionally, each year the USGS withholds data on certain limestone and dolomite end-uses due to confidentiality agreements regarding company proprietary data. For the purposes of this analysis, emissive end-uses that contained withheld data were estimated using one of the following techniques: (1) the value for all the withheld data points for limestone or dolomite use was distributed evenly to all withheld end-uses; (2) the average percent of total limestone or dolomite for the withheld end-use in the preceding and succeeding years; or (3) the average fraction of total limestone or dolomite for the end-use over the entire time period.

Finally, there is a large quantity of crushed stone reported to the USGS under the category "unspecified uses." A portion of this consumption is believed to be limestone or dolomite used for emissive end uses. The quantity listed for "unspecified uses" was, therefore, allocated to each reported end-use according to each end uses fraction of total consumption in that year.[7]

Table 4-24: Limestone and Dolomite Consumption (Thousand Metric Tons)

Activity	**1990**	**1997**	**1998**	**1999**	**2000**	**2001**	**2002**	**2003**
Flux Stone	6,738	11,226	11,514	13,390	6,248	5,558	5,275	4,501
Limestone	5,804	9,007	9,767	9,694	4,113	3,727	3,023	2,055
Dolomite	933	2,219	1,748	3,696	2,135	1,831	2,252	2,466
Glass Making	489	725	340	0	836	258	139	765
Limestone	430	725	149	0	836	258	139	765
Dolomite	59	0	191	0	0	0	0	0
FGD	3,258	3,242	2,795	2,819	4,030	5,798	6,286	4,390
Other Miscellaneous Uses	1,835	898	1,933	1,620	2,080	1,138	1,483	863
Total	**12,319**	**16,091**	**16,582**	**17,830**	**13,194**	**12,751**	**13,183**	**10,520**

Note: "Other miscellaneous uses" includes chemical stone, mine dusting or acid water treatment, acid neutralization, and sugar refining.

Table 4-25: Dolomitic Magnesium Metal Production Capacity (Metric Tons)

Year	**Production Capacity**
1990	35,000
1991	35,000
1992	14,909
1993	12,964
1994	21,111
1995	22,222
1996	40,000
1997	40,000
1998	40,000
1999	40,000
2000	40,000
2001	29,167
2002	0
2003	0

Note: Production capacity for 2002 and 2003 amount to zero because the last U.S. production plant employing the dolomitic process shut down mid-2001 (USGS 2002).

Uncertainty

Uncertainties in this estimate are due, in part, to variations in the chemical composition of limestone. In addition to calcium carbonate, limestone may contain smaller amounts of magnesia, silica, and sulfur. The exact specifications for limestone or dolomite used as flux stone vary with the pyrometallurgical process, the kind of ore processed, and the final use of the slag. Similarly, the quality of the limestone used for glass manufacturing will depend on the type of glass being manufactured.

Uncertainties also exist in the activity data. Much of the limestone consumed in the United States is reported as "other unspecified uses;" therefore, it is difficult to accurately allocate this unspecified quantity to the correct end-uses. Also, some of the limestone reported as "limestone" is believed to actually be dolomite, which has a higher carbon content. Additionally, there is significant inherent uncertainty associated with estimating withheld data points for specific end uses of limestone and dolomite. Lastly, the uncertainty of the estimates for limestone used in

[7] This approach was recommended by USGS.

glass making is especially high. Large fluctuations in reported consumption exist, reflecting year-to-year changes in the number of survey responders. The uncertainty resulting from a shifting survey population is exacerbated by the gaps in the time series of reports. However, since glass making accounts for a small percent of consumption, its contribution to the overall emissions estimate is low.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-26. Limestone and Dolomite Use CO_2 emissions were estimated to be between 4.4 and 5.1 Tg CO_2 Eq. at the 95 percent confidence level (or in 19 out of 20 Monte Carlo Stochastic Simulations). This indicates a range of approximately 7 percent below and 8 percent above the emission estimate of 4.7 Tg CO_2 Eq.

Table 4-26: Tier 2 Quantitative Uncertainty Estimates for CO_2 Emissions from Limestone and Dolomite Use (Tg CO_2 Eq. and Percent)

Source	**Gas**	**2003 Emission Estimate (Tg CO_2 Eq.)**	**Uncertainty Range Relative to Emission Estimate[a] (Tg CO_2 Eq.)**		**(%)**	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Limestone and Dolomite Use	CO_2	4.7	4.4	5.1	-7%	+8%

[a] Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

Recalculations Discussion

A spreadsheet error was corrected for the limestone and dolomite use emission estimate for 2002. The change resulted in an increase of less than 0.1 Tg CO_2 Eq. (0.8 percent) in CO_2 emissions from limestone and dolomite use for that year.

4.6. Soda Ash Manufacture and Consumption (IPCC Source Category 2A4)

Soda ash (sodium carbonate, Na_2CO_3) is a white crystalline solid that is readily soluble in water and strongly alkaline. Commercial soda ash is used as a raw material in a variety of industrial processes and in many familiar consumer products such as glass, soap and detergents, paper, textiles, and food. It is used primarily as an alkali, either in glass manufacturing or simply as a material that reacts with and neutralizes acids or acidic substances. Internationally, two types of soda ash are produced—natural and synthetic. The United States produces only natural soda ash and is the largest soda ash-producing country in the world. Trona is the principal ore from which natural soda ash is made.

Only three states produce natural soda ash: Wyoming, California, and Colorado. Of these three states, only net emissions of CO_2 from Wyoming were calculated. This difference is a result of the production processes employed in each state.[8] During the production process used in Wyoming, trona ore is treated to produce soda ash. Carbon dioxide is generated as a by-product of this reaction, and is eventually emitted into the atmosphere. In addition, CO_2 may also be released when soda ash is consumed.

In 2003, CO_2 emissions from the manufacture of soda ash from trona were approximately 1.5 Tg CO_2 Eq. (1,509 Gg). Soda ash consumption in the United States generated 2.6 Tg CO_2 Eq. (2,573 Gg) in 2003. Total emissions from soda ash manufacture in 2003 were 4.1 Tg CO_2 Eq. (4,082 Gg) (see Table 4-27 and Table 4-28). Emissions

[8] In California, soda ash is manufactured using sodium carbonate-bearing brines instead of trona ore. To extract the sodium carbonate, the complex brines are first treated with CO_2 in carbonation towers to convert the sodium carbonate into sodium bicarbonate, which then precipitates from the brine solution. The precipitated sodium bicarbonate is then calcined back into sodium carbonate. Although CO_2 is generated as a by-product, the CO_2 is recovered and recycled for use in the carbonation stage and is not emitted.

have fluctuated since 1990. These fluctuations were strongly related to the behavior of the export market and the U.S. economy. Emissions in 2003 decreased by approximately 1 percent from the previous year, and have decreased overall by approximately 1 percent since 1990.

Table 4-27: CO_2 Emissions from Soda Ash Manufacture and Consumption (Tg CO_2 Eq.)

Year	Manufacture	Consumption	Total
1990	1.4	2.7	4.1
1997	1.7	2.7	4.4
1998	1.6	2.7	4.3
1999	1.5	2.7	4.2
2000	1.5	2.7	4.2
2001	1.5	2.6	4.1
2002	1.5	2.7	4.1
2003	1.5	2.6	4.1

Note: Totals may not sum due to independent rounding.

Table 4-28: CO_2 Emissions from Soda Ash Manufacture and Consumption (Gg)

Year	Manufacture	Consumption	Total
1990	1,431	2,710	4,141
1997	1,665	2,689	4,354
1998	1,607	2,718	4,325
1999	1,548	2,668	4,217
2000	1,529	2,652	4,181
2001	1,500	2,648	4,147
2002	1,470	2,668	4,139
2003	1,509	2,573	4,082

Note: Totals may not sum due to independent rounding.

The United States has the world's largest deposits of trona and represents about one-third of total world soda ash output. The distribution of soda ash by end-use in 2003 was glass making, 49 percent; chemical production, 26 percent; soap and detergent manufacturing, 11 percent; distributors, five percent; flue gas desulfurization, pulp and paper production, two percent each; water treatment, one percent; and miscellaneous, four percent (USGS 2004).

Although the United States continues to be the major supplier of world soda ash, China's soda ash manufacturing capacity is rapidly increasing and is expected to surpass that of the United States. This will likely cause greater competition in Asian markets in the future. The world market for soda ash is expected to grow 1.5 to 2 percent annually (USGS 2004).

Methodology

During the production process, trona ore is calcined in a rotary kiln and chemically transformed into a crude soda ash that requires further processing. Carbon dioxide and water are generated as by-products of the calcination process. Carbon dioxide emissions from the calcination of trona can be estimated based on the following chemical reaction:

$$2(Na_3H(CO_3)_2 \cdot 2H_2O) \rightarrow 3Na_2CO_3 + 5H_2O + CO_2$$

[trona] [soda ash]

Based on this formula, approximately 10.27 metric tons of trona are required to generate one metric ton of CO_2. Thus, the 15.5 million metric tons of trona mined in 2003 for soda ash production (USGS 2004) resulted in CO_2 emissions of approximately 1.5 Tg CO_2 Eq. (1,509 Gg).

Once manufactured, most soda ash is consumed in glass and chemical production, with minor amounts in soap and detergents, pulp and paper, flue gas desulfurization and water treatment. As soda ash is consumed for these purposes, additional CO_2 is usually emitted. In these applications, it is assumed that one mole of carbon is released for every mole of soda ash used. Thus, approximately 0.113 metric tons of carbon (or 0.415 metric tons of CO_2) are released for every metric ton of soda ash consumed.

The activity data for trona production and soda ash consumption (see Table 4-29) were taken from USGS (1994 through 2004). Soda ash manufacture and consumption data were collected by the USGS from voluntary surveys of the U.S. soda ash industry.

Table 4-29: Soda Ash Manufacture and Consumption (Gg)

Year	Manufacture*	Consumption
1990	14,700	6,530
1991	14,700	6,280
1992	14,900	6,320
1993	14,500	6,280
1994	14,600	6,260
1995	16,500	6,500
1996	16,300	6,390
1997	17,100	6,480
1998	16,500	6,550
1999	15,900	6,430
2000	15,700	6,390
2001	15,400	6,380
2002	15,100	6,430
2003	15,500	6,200

* Soda ash manufactured from trona ore only.

Uncertainty

Emission estimates from soda ash manufacture are considered to have low associated uncertainty. Both the emission factor and activity data are reliable. However, emissions from soda ash consumption are dependent upon the type of processing employed by each end-use. Specific information characterizing the emissions from each end-use is limited. Therefore, there is uncertainty surrounding the emission factors from the consumption of soda ash.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-30. Soda Ash Manufacture and Consumption CO_2 emissions were estimated to be between 3.9 and 4.2 Tg CO_2 Eq. at the 95 percent confidence level (or in 19 out of 20 Monte Carlo Stochastic Simulations). This indicates a range of approximately 4 percent below and 4 percent above the emission estimate of 4.1 Tg CO_2 Eq.

Table 4-30: Tier 2 Quantitative Uncertainty Estimates for CO_2 Emissions from Soda Ash Manufacture and Consumption (Tg CO_2 Eq. and Percent)

Source	Gas	2003 Emission Estimate (Tg CO_2 Eq.)	Uncertainty Range Relative to Emission Estimate[a] (Tg CO_2 Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Soda Ash Manufacture and Consumption	CO_2	4.1	3.9	4.2	-4%	+4%

[a] Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

Planned Improvements

Emissions from soda ash production in Colorado, which is produced using the nahcolite production process, will be investigated for inclusion in future inventories.

4.7. Titanium Dioxide Production (IPCC Source Category 2B5)

Titanium dioxide (TiO_2) is a metal oxide manufactured from titanium ore, and is principally used as a pigment. Titanium dioxide is a principal ingredient in white paint, and TiO_2 is also used as a pigment in the manufacture of white paper, foods, and other products. There are two processes for making TiO_2, the chloride process and the sulfate process. Carbon dioxide is emitted from the chloride process, which uses petroleum coke and chlorine as raw materials and emits process-related CO_2. The sulfate process does not use petroleum coke or other forms of carbon as a raw material and does not emit CO_2.

The chloride process is based on the following chemical reactions:

$$2\ FeTiO_3 + 7\ Cl_2 + 3\ C \rightarrow 2\ TiCl_4 + 2\ FeCl_3 + 3\ CO_2$$

$$2\ TiCl_4 + 2\ O_2 \rightarrow 2\ TiO_2 + 4\ Cl_2$$

The carbon in the first chemical reaction is provided by petroleum coke, which is oxidized in the presence of the chlorine and $FeTiO_3$ (the Ti-containing ore) to form CO_2. The majority of U.S. TiO_2 was produced in the United States through the chloride process, and a special grade of petroleum coke is manufactured specifically for this purpose. Emissions of CO_2 from titanium dioxide production in 2003 were 2.0 Tg CO_2 Eq. (2,013 Gg), an increase of less than one percent from the previous year and 54 percent from 1990, due to increasing production within the industry (see Table 4-31).

Table 4-31: CO_2 Emissions from Titanium Dioxide (Tg CO_2 Eq. and Gg)

Year	Tg CO_2 Eq.	Gg
1990	1.3	1,308
1997	1.8	1,836
1998	1.8	1,819
1999	1.9	1,853
2000	1.9	1,918
2001	1.9	1,857
2002	2.0	1,997
2003	2.0	2,013

Methodology

Emissions of CO_2 from titanium dioxide production were calculated by multiplying annual titanium dioxide production by chlorine process-specific emission factors.

Data were obtained for the total amount of titanium dioxide produced each year, and it was assumed that 97 percent of the total production in 2003 was produced using the chloride process. It was assumed that titanium dioxide was produced using the chloride process and the sulfate process in the same ratio as the ratio of the total U.S. production capacity for each process. An emission factor of 0.4 metric tons C/metric ton TiO_2 was applied to the estimated chloride process production. It was assumed that all titanium dioxide produced using the chloride process was produced using petroleum coke, although some titanium dioxide may have been produced with graphite or other carbon inputs. The amount of petroleum coke consumed annually in titanium dioxide production was calculated based on the assumption that petroleum coke used in the process is 90 percent carbon and 10 percent inert materials.

The emission factor for the titanium dioxide chloride process was taken from the report, *Everything You've Always Wanted to Know about Petroleum Coke* (Onder and Bagdoyan 1993). Titanium dioxide production data for 1990 through 2003 (see Table 4-32) were obtained from personal communication with Joseph Gambogi, USGS Commodity Specialist, of the USGS (Gambogi 2004) and through the *Minerals Yearbook: Titanium Annual Report* (USGS 1991 through 2003). Data for the percentage of the total titanium dioxide production capacity that is chloride process for 1994 through 2002 were also taken from the USGS *Minerals Yearbook* and from Joseph Gambogi for 2003. Percentage chloride process data were not available for 1990 through 1993, and data from the 1994 USGS *Minerals Yearbook* were used for these years. Because a sulfate-process plant closed in September 2001, the chloride process percentage for 2001 was estimated based on a discussion with Joseph Gambogi (2002). By 2002, only one sulfate plant remained online in the United States. The composition data for petroleum coke were obtained from Onder and Bagdoyan (1993).

Table 4-32: Titanium Dioxide Production (Gg)

Year	Gg
1990	979
1991	992
1992	1,140
1993	1,160
1994	1,250
1995	1,250
1996	1,230
1997	1,340
1998	1,330
1999	1,350
2000	1,400
2001	1,330
2002	1,410
2003	1,420

Uncertainty

Although some titanium dioxide may be produced using graphite or other carbon inputs, information and data regarding these practices were not available. Titanium dioxide produced using graphite inputs may generate differing amounts of CO_2 per unit of titanium dioxide produced compared to the use of petroleum coke. The most accurate method for these estimates would be basing calculations on the amount of reducing agent used in the process, rather than the amount of titanium dioxide produced. These data were not available, however.

Also, annual titanium production is not reported by USGS by the type of production process used (chloride or sulfate). Only the percentage of total production capacity is reported. It was assumed that titanium dioxide was produced using the chloride process and the sulfate process in the same ratio as the ratio of the total U.S. production capacity for each process. This assumes that the chloride process plants and sulfate process plants operate at the same level of utilization. Finally, the emission factor was applied uniformly to all chloride process production, and no data were available to account for differences in production efficiency among chloride process plants. In calculating the amount of petroleum coke consumed in chloride process titanium dioxide production, literature data were used for petroleum coke composition. Certain grades of petroleum coke are manufactured specifically for use in the titanium dioxide chloride process; however, this composition information was not available.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-33. Titanium Dioxide Consumption CO_2 emissions were estimated to be between 1.7 and 2.3 Tg CO_2 Eq. at the 95 percent confidence level (or in 19 out of 20 Monte Carlo Stochastic Simulations). This indicates a range of approximately 16 percent below and 16 percent above the emission estimate of 2.0 Tg CO_2 Eq.

Table 4-33: Tier 2 Quantitative Uncertainty Estimates for CO_2 Emissions from Titanium Dioxide Production (Tg CO_2 Eq. and Percent)

Source	Gas	2003 Emission Estimate (Tg CO_2 Eq.)	Uncertainty Range Relative to Emission Estimate[a] (Tg CO_2 Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Titanium Dioxide Production	CO_2	2.0	1.7	2.3	-16%	+16%

[a] Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

4.8. Phosphoric Acid Production (IPCC Source Category 2A7)

Phosphoric acid [H_3PO_4] is a basic raw material in the production of phosphate-based fertilizers. Phosphate rock is mined in Florida, North Carolina, Idaho, Utah, and other areas of the United States and is used primarily as a raw material for phosphoric acid production. The production of phosphoric acid from phosphate rock produces byproduct gypsum [$CaSO_4$-$2H_2O$], referred to as phosphogypsum.

The composition of natural phosphate rock varies depending upon the location where it is mined. Natural phosphate rock mined in the United States generally contains inorganic carbon in the form of calcium carbonate (limestone) and also may contain organic carbon. The chemical composition of phosphate rock (francolite) mined in Florida is:

$$Ca_{10-x-y}\ Na_x\ Mg_y\ (PO_4)_{6-x}(CO_3)_xF_{2+0.4x}$$

The calcium carbonate component of the phosphate rock is integral to the phosphate rock chemistry. Phosphate rock can also contain organic carbon that is physically incorporated into the mined rock but is not an integral component of the phosphate rock chemistry. Phosphoric acid production from natural phosphate rock is a source of CO_2 emissions, due to the chemical reaction of the inorganic carbon (calcium carbonate) component of the phosphate rock.

The phosphoric acid production process involves chemical reaction of the calcium phosphate ($Ca_3(PO_4)_2$) component of the phosphate rock with sulfuric acid (H_2SO_4) and recirculated phosphoric acid (H_3PO_4) (EFMA 1997). The primary chemical reactions for the production of phosphoric acid from phosphate rock are:

$$Ca_3(PO_4)_2 + 4H_3PO_4 \rightarrow 3Ca(H_2PO_4)_2$$

$$3Ca(H_2PO_4)_2 + 3H_2SO_4 + 6H_2O \rightarrow 3CaSO_4\ 6H_2O + 6H_3PO_4$$

The limestone ($CaCO_3$) component of the phosphate rock reacts with the sulfuric acid in the phosphoric acid production process to produce calcium sulfate (phosphogypsum) and carbon dioxide. The chemical reaction for the limestone–sulfuric acid reaction is:

$$CaCO_3 + H_2SO_4 + H_2O \rightarrow CaSO_4\ 2H_2O + CO_2$$

Total marketable phosphate rock production in 2003 was 38.7 million metric tons. Approximately 86 percent of domestic phosphate rock production was mined in Florida and North Carolina, while approximately 14 percent of production was mined in Idaho and Utah. Florida alone represented more than 75 percent of domestic production. In addition, 2.4 million metric tons of crude phosphate rock was imported for consumption in 2003. Marketable phosphate rock production, including domestic production and imports for consumption, increased by approximately 3.7 percent between 2002 and 2003. However, over the 1990 to 2003 period, production decreased by 12 percent. The 35.3 million metric tons produced in 2001 was the lowest production level recorded since 1965 and was driven by a worldwide decrease in demand for phosphate fertilizers. Total CO_2 emissions from phosphoric acid production were 1.4 Tg CO_2 Eq. (1,382 Gg) in 2003 (see Table 4-34).

Table 4-34: CO_2 Emissions from Phosphoric Acid Production (Tg CO_2 Eq. and Gg)

Year	Tg CO_2 Eq.	Gg
1990	1.5	1,529
1997	1.5	1,544
1998	1.6	1,593
1999	1.5	1,539
2000	1.4	1,382
2001	1.3	1,264
2002	1.3	1,338
2003	1.4	1,382

Methodology

Carbon dioxide emissions from production of phosphoric acid from phosphate rock is calculated by multiplying the average amount of calcium carbonate contained in the natural phosphate rock by the amount of phosphate rock that is used annually to produce phosphoric acid, accounting for domestic production and net imports for consumption.

The USGS reports in the Minerals Yearbook, Phosphate Rock, the aggregate amount of phosphate rock mined annually in Florida and North Carolina and the aggregate amount of phosphate rock mined annually in Idaho and Utah, and reports the annual amounts of phosphate rock exported and imported for consumption (see Table 4-35). Data for domestic production of phosphate rock, exports of phosphate rock, and imports of phosphate rock for consumption for 1990 through 2003 were obtained from USGS Mineral Yearbook, Phosphate Rock (USGS 1994 through 2004).

The carbonate content of phosphate rock varies depending upon where the material is mined. Composition data for domestically mined and imported phosphate rock were provided by the Florida Institute of Phosphate Research (FIPR 2003). Phosphate rock mined in Florida contains approximately 3.5 percent inorganic carbon (as CO_2), and phosphate rock imported from Morocco contains approximately 5 percent inorganic carbon (as CO_2). Calcined phosphate rock mined in North Carolina and Idaho contains approximately 1.5 percent and 1.0 percent inorganic carbon (as CO_2), respectively (see Table 4-36).

Carbonate content data for phosphate rock mined in Florida are used to calculate the CO_2 emissions from consumption of phosphate rock mined in Florida and North Carolina (86 percent of domestic production) and carbonate content data for phosphate rock mined in Morocco are used to calculate CO_2 emissions from consumption of imported phosphate rock. The CO_2 emissions calculation is based on the assumption that all of the domestic production of phosphate rock is used in uncalcined form. The USGS reported that one phosphate rock producer in Idaho is producing calcined phosphate rock; however, no production data were available for this single producer (USGS 2003). Carbonate content data for uncalcined phosphate rock mined in Idaho and Utah (14 percent of domestic production) were not available, and carbonate content was therefore estimated from the carbonate content data for calcined phosphate rock mined in Idaho.

The CO_2 emissions calculation methodology is based on the assumption that all of the inorganic carbon (calcium carbonate) content of the phosphate rock reacts to CO_2 in the phosphoric acid production process and is emitted with the stack gas. The methodology also assumes that none of the organic carbon content of the phosphate rock is converted to CO_2 and that all of the organic carbon content remains in the phosphoric acid product.

Table 4-35: Phosphate Rock Domestic Production, Exports, and Imports (Gg)

Location/Year	1990	1997	1998	1999	2000	2001	2002	2003
U.S. Production								
FL & NC	42,494	36,604	38,000	35,900	31,900	28,100	29,800	31,300
ID & UT	7,306	5,496	5,640	5,540	5,470	4,730	4,920	5,100
Exports - FL & NC	6,240	335	378	272	299	9	62	64
Imports - Morocco	451	1,830	1,760	2,170	1,930	2,500	2,700	2,400
Total U.S. Consumption	**44,011**	**43,595**	**45,022**	**43,338**	**39,001**	**35,321**	**37,358**	**38,746**

Source: USGS 2004, 2003, 2002, 2001, 2000, 1999, 1998, 1997, 1996, 1995.

Table 4-36: Chemical Composition of Phosphate Rock (percent by weight)

Composition	Central Florida	North Florida	North Carolina (calcined)	Idaho (calcined)	Morocco
Total Carbon (as C)	1.60	1.76	0.76	0.60	1.56
Inorganic Carbon (as C)	1.0	0.93	0.41	0.27	1.46
Organic Carbon (as C)	0.60	0.83	0.35	—	0.1
Inorganic Carbon (as CO_2)	3.67	3.43	1.50	1.0	5.0

Source: FIPR 2003
(—): Assumed equal to zero.

Uncertainty

Phosphate rock production data used in the emission calculations are developed by the USGS through monthly and semiannual voluntary surveys of the eleven companies that owned phosphate rock mines during 2003. The phosphate rock production data are not considered to be a significant source of uncertainty, because all eleven of the domestic phosphate rock producers are reporting their annual production to the USGS. Data for imports for consumption and exports of phosphate rock used in the emission calculation are based on international trade data collected by the U.S. Census Bureau. These U.S. government economic data are not considered to be a significant source of uncertainty.

One source of potentially significant uncertainty in the calculation of CO_2 emissions from phosphoric acid production is the data for the carbonate composition of phosphate rock. The composition of phosphate rock varies depending upon where the material is mined, and may also vary over time. Only one set of data from the Florida Institute of Phosphate Research was available for the composition of phosphate rock mined domestically and imported, and data for uncalcined phosphate rock mined in North Carolina and Idaho were unavailable. Inorganic carbon content (as CO_2) of phosphate rock could vary ±1 percent from the data included in Table 4-36, resulting in a variation in CO_2 emissions of ±20 percent. Another source of uncertainty is the disposition of the organic carbon content of the phosphate rock. A representative of the FIPR indicated that in the phosphoric acid production process the organic carbon content of the mined phosphate rock generally remains in the phosphoric acid product, which is what produces the color of the phosphoric acid product (FIPR 2003a). Organic carbon is therefore not included in the calculation of CO_2 emissions from phosphoric acid production. However, if, for example, 50 percent of the organic carbon content of the phosphate rock were to be emitted as CO_2 in the phosphoric acid production process, the CO_2 emission estimate would increase by on the order of 50 percent.

A third source of uncertainty is the assumption that all domestically-produced phosphate rock is used in phosphoric acid production and used without first being calcined. Calcination of the phosphate rock would result in conversion of some of the organic carbon in the phosphate rock into CO_2. However, according to the USGS, only one producer in Idaho is currently calcining phosphate rock, and no data were available concerning the annual production of this single producer (USGS 2003). Total production of phosphate rock in Utah and Idaho combined amounts to approximately 14 percent of total domestic production in 2003. If it is assumed that 100 percent of the reported domestic production of phosphate rock for Idaho and Utah was first calcined, and it is assumed that 50 percent of the organic carbon content of the total production for Idaho and Utah was converted to CO_2 in the calcination process, the CO_2 emission estimate would increase on the order of 10 percent.

Finally, USGS indicated that 5 percent of domestically-produced phosphate rock is used to manufacture elemental phosphorus and other phosphorus-based chemicals, rather than phosphoric acid (USGS 2003a). According to USGS, there is only one domestic producer of elemental phosphorus, in Idaho, and no data were available concerning the annual production of this single producer. Elemental phosphorus is produced by reducing phosphate rock with coal coke, and it is therefore assumed that 100 percent of the carbonate content of the phosphate rock will be converted to CO_2 in the elemental phosphorus production process. The calculation for CO_2 emissions is based on the assumption that phosphate rock consumption, for purposes other than phosphoric acid production, results in CO_2 emissions from 100 percent of the inorganic carbon content in phosphate rock, but none from the organic carbon content. This phosphate rock, consumed for other purposes, constitutes approximately 5 percent of total phosphate rock consumption. If it were assumed that there are zero emissions from other uses of phosphate rock, CO_2 emissions would fall 5 percent.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-37. Phosphoric acid production CO_2 emissions were estimated to be between 1.1 and 1.6 Tg CO_2 Eq. at the 95 percent confidence level (or in 19 out of 20 Monte Carlo Stochastic Simulations). This indicates a range of approximately 18 percent below and 18 percent above the emission estimate of 1.4 Tg CO_2 Eq.

Table 4-37: Tier 2 Quantitative Uncertainty Estimates for CO_2 Emissions from Phosphoric Acid Production (Tg CO_2 Eq. and Percent)

Source	Gas	2003 Emission Estimate (Tg CO_2 Eq.)	Uncertainty Range Relative to Emission Estimate[a]			
			(Tg CO_2 Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Phosphoric Acid Production	CO_2	1.4	1.1	1.6	-18%	+18%

[a] Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

Recalculations Discussion

The historical activity data used to calculate the emissions from phosphoric acid production were updated for the year 2002. The change resulted in a decrease of less than 0.1 Tg CO_2 Eq. (less than 0.1 percent) in CO_2 emissions from phosphoric acid production for that year.

Planned Improvements

The estimate of CO_2 emissions from phosphoric acid production could be improved through collection of additional data. Additional data is being collected concerning the carbonate content of uncalcined phosphate rock mined in various locations in the United States. Additional research will also be conducted concerning the disposition of the organic carbon content of the phosphate rock in the phosphoric acid production process. Only a single producer of phosphate rock is calcining the product, and only a single producer is manufacturing elemental phosphorus. Annual production data for these single producers will probably remain unavailable.

4.9. Ferroalloy Production (IPCC Source Category 2C2)

Carbon dioxide is emitted from the production of several ferroalloys. Ferroalloys are composites of iron and other elements such as silicon, manganese, and chromium. When incorporated in alloy steels, ferroalloys are used to alter the material properties of the steel. Estimates from two types of ferrosilicon (25 to 55 percent and 56 to 95 percent silicon), silicon metal (about 98 percent silicon), and miscellaneous alloys (36 to 65 percent silicon) have been calculated. Emissions from the production of ferrochromium and ferromanganese are not included here because of the small number of manufacturers of these materials in the United States. Subsequently, government information disclosure rules prevent the publication of production data for these production facilities. Similar to emissions from the production of iron and steel, CO_2 is emitted when metallurgical coke is oxidized during a high-temperature reaction with iron and the selected alloying element. Due to the strong reducing environment, CO is initially produced, and eventually oxidized to CO_2. A representative reaction equation for the production of 50 percent ferrosilicon is given below:

$$\mathrm{Fe_2O_3 + 2SiO_2 + 7C \rightarrow 2FeSi + 7CO}$$

Emissions of CO_2 from ferroalloy production in 2003 were 1.4 Tg CO_2 Eq. (1,374 Gg) (see Table 4-38), an 11 percent increase from the previous year and a 31 percent reduction since 1990.

Table 4-38: CO_2 Emissions from Ferroalloy Production (Tg CO_2 Eq. and Gg)

Year	Tg CO_2 Eq.	Gg
1990	2.0	1,980
1997	2.0	2,038
1998	2.0	2,027
1999	2.0	1,996
2000	1.7	1,719
2001	1.3	1,329
2002	1.2	1,237
2003	1.4	1,374

Methodology

Emissions of CO_2 from ferroalloy production were calculated by multiplying annual ferroalloy production by material-specific emission factors. Emission factors taken from the *Revised 1996 IPCC Guidelines* (IPCC/UNEP/OECD/IEA 1997) were applied to ferroalloy production. For ferrosilicon alloys containing 25 to 55 percent silicon and miscellaneous alloys (including primarily magnesium-ferrosilicon, but also including other silicon alloys) containing 32 to 65 percent silicon, an emission factor for 50 percent silicon ferrosilicon (2.35 tons CO_2/ton of alloy produced) was applied. Additionally, for ferrosilicon alloys containing 56 to 95 percent silicon, an emission factor for 75 percent silicon ferrosilicon (3.9 tons CO_2 per ton alloy produced) was applied. The emission factor for silicon metal was assumed to be 4.3 tons CO_2/ton metal produced. It was assumed that 100 percent of the ferroalloy production was produced using petroleum coke using an electric arc furnace process (IPCC/UNEP/OECD/IEA 1997), although some ferroalloys may have been produced with coking coal, wood, other biomass, or graphite carbon inputs. The amount of petroleum coke consumed in ferroalloy production was calculated assuming that the petroleum coke used is 90 percent carbon and 10 percent inert material.

Ferroalloy production data for 1990 through 2003 (see Table 4-39) were obtained from the USGS through personal communications with Lisa Corathers (2004), the Silicon Commodity Specialist, and through the *Minerals Yearbook: Silicon Annual Report* (USGS 1991, 1992, 1993, 1994, 1995, 1996, 1997, 1998, 1999, 2000, 2001, 2002, 2003). Until 1999, the USGS reported production of ferrosilicon containing 25 to 55 percent silicon separately from production of miscellaneous alloys containing 32 to 65 percent silicon; beginning in 1999, the USGS reported these as a single category (see Table 4-39). The composition data for petroleum coke was obtained from Onder and Bagdoyan (1993).

Table 4-39: Production of Ferroalloys (Metric Tons)

Year	Ferrosilicon 25%-55%	Ferrosilicon 56%-95%	Silicon Metal	Misc. Alloys (32-65%)
1990	321,385	109,566	145,744	72,442
1997	175,000	147,000	187,000	106,000
1998	162,000	147,000	195,000	99,800
1999	252,000	145,000	195,000	NA
2000	229,000	100,000	184,000	NA
2001	167,000	89,000	137,000	NA
2002	156,000	98,600	113,000	NA
2003	113,000	75,800	189,000	NA

NA (Not Available)

Uncertainty

Although some ferroalloys may be produced using wood or other biomass as a carbon source, information and data regarding these practices were not available. Emissions from ferroalloys produced with wood or other biomass would not be counted under this source because wood-based carbon is of biogenic origin.[9] Even though emissions from ferroalloys produced with coking coal or graphite inputs would be counted in national trends, they may be generated with varying amounts of CO_2 per unit of ferroalloy produced. The most accurate method for these estimates would be to base calculations on the amount of reducing agent used in the process, rather than the amount of ferroalloys produced. These data, however, were not available.

Also, annual ferroalloy production is now reported by the USGS in three broad categories: ferroalloys containing 25 to 55 percent silicon (including miscellaneous alloys), ferroalloys containing 56 to 95 percent silicon, and silicon metal. It was assumed that the IPCC emission factors apply to all of the ferroalloy production processes, including miscellaneous alloys. Finally, production data for silvery pig iron (alloys containing less than 25 percent silicon) are not reported by the USGS to avoid disclosing company proprietary data. Emissions from this production category, therefore, were not estimated.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-40. Ferroalloy Production CO_2 emissions were estimated to be between 1.3 and 1.4 Tg CO_2 Eq. at the 95 percent confidence level (or in 19 out of 20 Monte Carlo Stochastic Simulations). This indicates a range of approximately 3 percent below and 3 percent above the emission estimate of 1.4 Tg CO_2 Eq.

Table 4-40: Tier 2 Quantitative Uncertainty Estimates for CO_2 Emissions from Ferroalloy Production (Tg CO_2 Eq. and Percent)

Source	Gas	2003 Emission Estimate (Tg CO_2 Eq.)	Uncertainty Range Relative to Emission Estimate[a] (Tg CO_2 Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Ferroalloy Production	CO_2	1.4	1.3	1.4	-3%	+3%

[a] Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

4.10. Carbon Dioxide Consumption (IPCC Source Category 2B5)

Carbon dioxide (CO_2) is used for a variety of commercial applications, including food processing, chemical production, carbonated beverage production, and refrigeration, and is also used in petroleum production for enhanced oil recovery (EOR). Carbon dioxide used for EOR is injected into the underground reservoirs to increase the reservoir pressure to enable additional petroleum to be produced.

For the most part, CO_2 used in non-EOR applications will eventually be released to the atmosphere, and for the purposes of this analysis CO_2 used in commercial applications other than EOR is assumed to be emitted to the atmosphere. Carbon dioxide used in EOR applications is considered for the purposes of this analysis to remain sequestered in the underground formations into which the CO_2 is injected.

It is unclear to what extent the CO_2 used for EOR will be re-released to the atmosphere. Carbon dioxide used in EOR applications is compressed at the CO_2 production source, transported by pipeline to the EOR field, and injected into wellheads. Potential CO_2 leakage pathways from CO_2 production, transportation, and injection process include fugitive emissions from the compressors, pipeline equipment, and wellheads. Also, the CO_2 used for EOR may show up at the wellhead after a few years of injection (Hangebrauk et al. 1992) or may be partially recovered

[9] Emissions and sinks of biogenic carbon are accounted for in the Land-Use Change and Forestry chapter.

as a component of crude oil produced from the wells (Denbury Resources 2003a). This CO_2 may be recovered and re-injected into the wellhead or separated from the petroleum produced and vented to the atmosphere. More research is required to determine the amount of CO_2 that may escape from EOR operations through leakage from equipment, as a component of the crude oil produced, or as leakage directly from the reservoir through geologic faults and fractures or through improperly plugged or improperly completed wells. For the purposes of this analysis, it is assumed that all of the CO_2 produced for use in EOR applications is injected into reservoirs (i.e., there is no loss of CO_2 to the atmosphere during CO_2 production, transportation, or injection for EOR applications) and that all of the injected CO_2 remains sequestered within the reservoirs.

Carbon dioxide is produced from naturally occurring CO_2 reservoirs, as a by-product from the energy and industrial production processes (e.g., ammonia production, fossil fuel combustion, ethanol production), and as a by-product from the production of crude oil and natural gas, which contain naturally occurring CO_2 as a component. Carbon dioxide produced from naturally occurring CO_2 reservoirs and used in industrial applications other than EOR is included in this analysis. Neither by-product CO_2 generated from energy or industrial production processes nor CO_2 separated from crude oil and natural gas are included in this analysis for a number of reasons.

Depending on the raw materials that are used, by-product CO_2 generated during energy and industrial production processes may already be accounted for in the CO_2 emission estimates from fossil fuel consumption (either from fossil fuel combustion or from non-energy uses of fossil fuels). For example, ammonia is primarily manufactured using natural gas as both a feedstock and energy source. Carbon dioxide emissions from natural gas combustion for ammonia production are accounted for in the CO_2 from Fossil Fuel Combustion source category of the Energy sector and, therefore, are not included under Carbon Dioxide Consumption. Likewise, CO_2 emissions from natural gas used as feedstock for ammonia production are accounted for in this chapter under the Ammonia Manufacture source category and, therefore, are not included here.[10]

Carbon dioxide is produced as a by-product of crude oil and natural gas production. This CO_2 is separated from the crude oil and natural gas using gas processing equipment, and may be emitted directly to the atmosphere, or captured and reinjected into underground formations, used for EOR, or sold for other commercial uses. The amount of CO_2 separated from crude oil and natural gas has not been estimated.[11] Therefore, the only CO_2 consumption that is accounted for in this analysis is CO_2 produced from natural wells other than crude oil and natural gas wells that is used in commercial applications other than EOR.

There are currently two facilities, one in Mississippi and one in New Mexico, producing CO_2 from natural CO_2 reservoirs for use in both EOR and in other commercial applications (e.g., chemical manufacturing, food production). There are other naturally occurring CO_2 reservoirs, mostly located in the western U.S. Facilities are producing CO_2 from these natural reservoirs, but they are only producing CO_2 for EOR applications, not for other commercial applications (Allis, R. et al. 2000). In 2003, the amount of CO_2 produced by the Mississippi and New Mexico facilities for commercial applications and subsequently emitted to the atmosphere were 1.3 Tg CO_2 Eq. (1,267 Gg) (see Table 4-41). This amount represents an increase of 29 percent from the previous year and an increase of 47 percent from emissions in 1990. This increase was due to an increase in the Mississippi facility's reported production for use in other commercial applications.

Table 4-41: CO_2 Emissions from Carbon Dioxide Consumption (Tg CO_2 Eq. and Gg)

Year	Tg CO_2 Eq.	Gg

[10] One ammonia manufacturer located in Oklahoma is reportedly capturing approximately 35 MMCF/day (0.67 Tg/yr) of by-product CO_2 for use in EOR applications. According to the methodology used in this analysis, this amount of CO_2 would be considered to be sequestered and not emitted to the atmosphere. However, time series data for the amount of CO_2 captured from the ammonia plant for use in EOR applications are not available, and therefore all of the CO_2 produced by the ammonia plant is assumed to be emitted to the atmosphere and is accounted for in this chapter under Ammonia Manufacture.

[11] The United States is in the process of developing a methodology to account for CO_2 emissions from natural gas systems and petroleum systems for inclusion in future Inventory submissions. For more information see Annex 5.

1990	0.9	860
1997	0.8	808
1998	0.9	912
1999	0.8	849
2000	1.0	957
2001	0.8	818
2002	1.0	979
2003	1.3	1,267

Methodology

Carbon dioxide emission estimates for 2001, 2002, and 2003 were based on production data for the two facilities currently producing CO_2 from naturally-occurring CO_2 reservoirs. Some of the CO_2 produced by these facilities is used for EOR and some is used in other commercial applications (e.g., chemical manufacturing, food production). Carbon dioxide produced from these two facilities that was used for EOR is assumed to remain sequestered and is not included in the CO_2 emissions totals. It is assumed that 100 percent of the CO_2 production used in commercial applications other than EOR is eventually released into the atmosphere.

Carbon dioxide production data for the Jackson Dome, Mississippi facility in 2001, 2002, and 2003 and the percentage of total production that was used for EOR and in non-EOR applications were obtained from the Annual Reports for Denbury Resources, the operator of the facility (Denbury Resources 2002, Denbury Resources 2003b, Denbury Resources 2004). Denbury Resources reported the average CO_2 production in units of MMCF CO_2 per day for 2001, 2002, and 2003, and reported the percentage of the total average annual production that was used for EOR. Carbon dioxide production data for the Bravo Dome, New Mexico facility were obtained from the New Mexico Bureau of Geology and Mineral Resources for the years 1990 through 2001 (Broadhead 2003). According to the New Mexico Bureau, the amount of CO_2 produced from Bravo Dome for use in non-EOR applications is less than one percent of total production (Broadhead 2003). Production data for 2002 and 2003 were not available for Bravo Dome, so it is assumed that the production values for those years are equal to the 2001 value.

Denbury Resources acquired the Jackson Dome facility in 2001 and CO_2 production data for the Jackson Dome facility are not available for years prior to 2001. Therefore, for 1990 through 2000, CO_2 emissions from CO_2 consumption in commercial applications other than EOR are estimated based on the total annual domestic consumption of CO_2 in commercial applications other than EOR in 2001 multiplied by the percentage of the total CO_2 consumed in commercial applications other than EOR that originated from CO_2 production at the Jackson Dome and Bravo Dome facilities in 2001. The total domestic commercial consumption of CO_2 in commercial applications other than EOR as reported by the U.S. Census Bureau was about 11,414 thousand metric tons in 2001. The total non-EOR CO_2 produced from the Jackson Dome and Bravo Dome natural reservoirs in 2001 was about 820 thousand metric tons, corresponding to 7.2 percent of the total domestic non-EOR commercial CO_2 consumption. This 7.2 percent factor was applied to the annual non-EOR commercial CO_2 consumption data for the years 1990 through 2000 to estimate annual CO_2 emissions from non-EOR commercial consumption of CO_2 produced from naturally occurring CO_2 reservoirs. The remaining 92.8 percent of the total annual non-EOR commercial CO_2 consumption is assumed to be accounted for in the CO_2 emission estimates from other categories (e.g., Ammonia Manufacture, CO_2 from Fossil Fuel Combustion, Wood Biomass and Ethanol Consumption).

Non-EOR commercial CO_2 consumption data (see Table 4-42) for years 1991 and 1992 were obtained from *Industry Report 1992* (U.S. Census 1993). Consumption data are not available for 1990, and therefore CO_2 consumption data for 1990 is assumed to be equal to that for 1991. Consumption data for 1993 and 1994 were obtained from *U.S. Census Bureau Manufacturing Profile, 1994* (U.S. Census 1995). Consumption data for 1996 through 2003 were obtained from the U.S. Census Bureau's *Industry Report, 1996, 1998, 2000, 2002, and 2003* (U.S. Census 1997, 1999, 2001, 2003, 2005).

Table 4-42: Carbon Dioxide Consumption (Metric Tons)

Year	Metric Tons
1990	11,997,726

1997	11,268,219
1998	12,716,070
1999	11,843,386
2000	13,354,262
2001	11,413,889
2002	11,313,478
2003	11,103,777

Uncertainty

Uncertainty exists in the assumption that 92.6 percent of the total domestic CO_2 production for commercial consumption other than EOR from 1990 through 2000 came from energy and industrial production processes, while 7.4 percent came from naturally occurring CO_2 reservoirs. The allocation for these years is assumed to be the same allocation as for 2001, the last year for which data are available to calculate the allocation.

Uncertainty also exists with respect to the number of facilities that are currently producing CO_2 from naturally occurring reservoirs for commercial uses other than EOR, and for which the CO_2 emissions are not accounted for elsewhere. Research indicates that there are only two such facilities, which are in New Mexico and Mississippi, however, additional facilities may exist that have not been identified. In addition, it is possible that CO_2 recovery exists in particular production and end-use sectors that are not accounted for elsewhere. Such recovery may or may not affect the overall estimate of CO_2 emissions from that sector depending upon the end use to which the recovered CO_2 is applied. For example, research has identified one ammonia production facility that is recovering CO_2 for use in EOR. Such CO_2 would be assumed to remain sequestered, however, time series data for the amount of recovered is not available and therefore all of the CO_2 produced by this plant is assumed to be emitted to the atmosphere and is allocated to Ammonia Manufacture. Recovery of CO_2 from ammonia production facilities for use in EOR is further discussed in this chapter under Ammonia Manufacture. Further research is required to determine whether CO_2 is being recovered from other facilities for application to end uses that are not accounted for elsewhere.

Uncertainty also exists in the assumption that 100 percent of the CO_2 used for EOR is sequestered. Operating experience with EOR systems indicates that 100 percent of the CO_2 used in EOR applications does not remain sequestered, but rather that it may be emitted to the atmosphere as leakage from equipment and reservoirs or recovered as a component of the crude oil produced. Potential sources of CO_2 emissions from EOR applications include leakage from equipment used to produce, transport, compress, and inject the CO_2, leakage from equipment used to process the crude oil produced, separate the CO_2 from the crude oil and recompress and recycle [reinject] the CO_2 recovered from the crude oil. Other potential sources of CO_2 emissions from EOR applications include leakage from the reservoir itself, either through migration of the injected CO_2 beyond the boundaries of the reservoir, chemical interactions between the injected CO_2 and the reservoir rock, and leakage via faults, fractures, oil and gas well bores, and water wells.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-43. Carbon dioxide consumption CO_2 emissions were estimated to be between 1.2 and 1.3 Tg CO_2 Eq. at the 95 percent confidence level (or in 19 out of 20 Monte Carlo Stochastic Simulations). This indicates a range of approximately 5 percent below to 5 percent above the emission estimate of 1.3 Tg CO_2 Eq.

Table 4-43: Tier 2 Quantitative Uncertainty Estimates for CO_2 Emissions from Carbon Dioxide Consumption (Tg CO_2 Eq. and Percent)

Source	**Gas**	**2003 Emission Estimate (Tg CO_2 Eq.)**	**Uncertainty Range Relative to Emission Estimate[a]**			
			(Tg CO_2 Eq.)		**(%)**	
			Lower Bound	**Upper Bound**	**Lower Bound**	**Upper Bound**
Carbon Dioxide Consumption	CO_2	1.3	1.2	1.3	-5%	+5%

[a] Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

Recalculations Discussion

Carbon dioxide consumption values were updated for 2001 for the Bravo Dome, and for both 2001 and 2002 for the Jackson Dome. For the Bravo Dome, updated values are based on new production data from the facility. For Jackson Dome, previous production data was based on fourth quarter reporting by Denbury Resources, which was annualized for the entire year. Updated production values are based on annual production numbers reported by Denbury Resources. For 2001, updated production values resulted in a 4 percent decrease in emissions, and for 2002 updated production values resulting in a 23 percent decrease in emissions. Based on updated 2001 consumption values for Jackson Dome, the percent of CO_2 emissions from CO_2 consumption in commercial applications other than EOR applied to years 1990 through 2000 decreased by 0.2 percent relative to the percent previously assumed. These changes resulted in an average annual decrease in CO_2 emissions from CO_2 consumption of less than 0.1 Tg CO_2 Eq. (5.1 percent) for the years 1990 through 2002.

4.11. Petrochemical Production (IPCC Source Category 2B5)

The production of some petrochemicals results in the release of small amounts of CH_4 and CO_2 emissions. Petrochemicals are chemicals isolated or derived from petroleum or natural gas. Methane emissions are presented here from the production of carbon black, ethylene, ethylene dichloride, styrene, and methanol, while CO_2 emissions are presented here for only carbon black production. The CO_2 emissions from petrochemical processes other than carbon black are currently included in the Carbon Stored in Products from Non-Energy Uses of Fossil Fuels Section of the Energy chapter. The CO_2 from carbon black production is included here to allow for the direct reporting of CO_2 emissions from the process and direct accounting of the feedstocks used in the process.

Carbon black is an intensely black powder generated by the incomplete combustion of an aromatic petroleum or coal-based feedstock. Most carbon black produced in the United States is added to rubber to impart strength and abrasion resistance, and the tire industry is by far the largest consumer. Ethylene is consumed in the production processes of the plastics industry including polymers such as high, low, and linear low density polyethylene (HDPE, LDPE, LLDPE), polyvinyl chloride (PVC), ethylene dichloride, ethylene oxide, and ethylbenzene. Ethylene dichloride is one of the first manufactured chlorinated hydrocarbons with reported production as early as 1795. In addition to being an important intermediate in the synthesis of chlorinated hydrocarbons, ethylene dichloride is used as an industrial solvent and as a fuel additive. Styrene is a common precursor for many plastics, rubber, and resins. It can be found in many construction products, such as foam insulation, vinyl flooring, and epoxy adhesives. Methanol is an alternative transportation fuel as well as a principle ingredient in windshield wiper fluid, paints, solvents, refrigerants, and disinfectants. In addition, methanol-based acetic acid is used in making PET plastics and polyester fibers. The United States produces close to one quarter of the world's supply of methanol.

Emissions of CO_2 and CH_4 from petrochemical production in 2003 were 2.8 Tg CO_2 Eq. (2,777 Gg) and 1.5 Tg CO_2 Eq. (72 Gg), respectively (see Table 4-44 and Table 4-45). While emissions of CO_2 from carbon black production in 2003 decreased by three percent from the previous year, there has been an overall increase in CO_2 emissions from carbon black production of 25 percent since 1990. Methane emissions from petrochemical production decreased by less than one percent from the previous year and increased 30 percent since 1990.

Table 4-44: CO_2 and CH_4 Emissions from Petrochemical Production (Tg CO_2 Eq.)

Year	1990		1997	1998	1999	2000	2001	2002	2003
CO_2	2.2		2.9	3.0	3.1	3.0	2.8	2.9	2.8
CH_4	1.2		1.6	1.7	1.7	1.7	1.4	1.5	1.5
Total	**3.4**		**4.6**	**4.7**	**4.8**	**4.7**	**4.2**	**4.4**	**4.3**

Table 4-45: CO_2 and CH_4 Emissions from Petrochemical Production (Gg)

Year	1990		1997	1998	1999	2000	2001	2002	2003
CO_2	2,221		2,919	3,015	3,054	3,004	2,787	2,857	2,777
CH_4	56		78	80	81	80	68	72	72

Methodology

Emissions of CH_4 were calculated by multiplying annual estimates of chemical production by the appropriate emission factor, as follows: 11 kg CH_4/metric ton carbon black, 1 kg CH_4/metric ton ethylene, 0.4 kg CH_4/metric ton ethylene dichloride,[12] 4 kg CH_4/metric ton styrene, and 2 kg CH_4/metric ton methanol. Although the production of other chemicals may also result in CH_4 emissions, there were not sufficient data available to estimate their emissions.

Emission factors were taken from the *Revised 1996 IPCC Guidelines* (IPCC/UNEP/OECD/IEA 1997). Annual production data for 1990 (see Table 4-46) were obtained from the Chemical Manufacturer's Association *Statistical Handbook* (CMA 1999). Production data for 1991 through 2003 were obtained from the American Chemistry Council's *Guide to the Business of Chemistry* (2003).

Table 4-46: Production of Selected Petrochemicals (Thousand Metric Tons)

Chemical	1990		1997	1998	1999	2000	2001	2002	2003
Carbon Black	1,307		1,719	1,775	1,798	1,769	1,641	1,682	1,635
Ethylene	16,542		23,088	23,474	25,118	24,971	22,521	23,623	22,957
Ethylene Dichloride	6,282		10,324	11,080	10,308	9,866	9,294	9,288	9,952
Styrene	3,637		5,171	5,183	5,410	5,420	4,277	4,974	5,239
Methanol	3,785		5,743	5,860	5,303	4,876	3,402	3,289	3,166

Almost all carbon black in the United States is produced from petroleum-based or coal-based feedstocks using the "furnace black" process (European IPPC Bureau 2004). The furnace black process is a partial combustion process in which a portion of the carbon black feedstock is combusted to provide energy to the process. Carbon black is also produced in the United States by the thermal cracking of acetylene-containing feedstocks ("acetylene black process") and by the thermal cracking of other hydrocarbons ("thermal black process"). One U.S. carbon black plant produces carbon black using the thermal black process, and one U.S. carbon black plant produces carbon black using the acetylene black process (The Innovation Group 2004).

The furnace black process produces carbon black from "carbon black feedstock" (also referred to as "carbon black oil"), which is a heavy aromatic oil that may be derived as a byproduct of either the petroleum refining process or the metallurgical (coal) coke production process. For the production of both petroleum-derived and coal-derived carbon black, the "primary feedstock" (i.e., carbon black feedstock) is injected into a furnace that is heated by a "secondary feedstock" (generally natural gas). Both the natural gas secondary feedstock and a portion of the carbon black feedstock are oxidized to provide heat to the production process and pyrolyze the remaining carbon black feedstock to carbon black. The "tail gas" from the furnace black process contains CO_2, carbon monoxide, sulfur compounds, CH_4, and non-methane volatile organic compounds. A portion of the tail gas is generally burned for energy recovery to heat the downstream carbon black product dryers. The remaining tail gas may also be burned for energy recovery, flared, or vented uncontrolled to the atmosphere.

The calculation of the carbon lost during the production process is the basis for determining the amount of CO_2 released during the process. The carbon content of national carbon black production is subtracted from the total amount of carbon contained in primary and secondary carbon black feedstock to find the amount of carbon lost during the production process. It is assumed that the carbon lost in this process is emitted to the atmosphere as either CH_4 or CO_2. The carbon content of the CH_4 emissions, estimated as described above, is subtracted from the total carbon lost in the process to calculate the amount of carbon emitted as CO_2. The total amount of primary and secondary carbon black feedstock consumed in the process (see Table 4-47) is estimated using a primary feedstock consumption factor and a secondary feedstock consumption factor estimated from U.S. Census Bureau (1999 and 2004) data. The average carbon black feedstock consumption factor for U.S. carbon black production is 1.43 metric

[12] The emission factor obtained from IPCC/UNEP/OECD/IEA (1997), page 2.23 is assumed to have a misprint; the chemical identified should be ethylene dichloride ($C_2H_4Cl_2$) rather than dichloroethylene ($C_2H_2Cl_2$).

tons of carbon black feedstock consumed per metric ton of carbon black produced. The average natural gas consumption factor for U.S. carbon black production is 341 normal cubic meters of natural gas consumed per metric ton of carbon black produced. The amount of carbon contained in the primary and secondary feedstocks is calculated by applying the respective carbon contents of the feedstocks to the respective levels of feedstock consumption.

Table 4-47: Carbon Black Feedstock (Primary Feedstock) and Natural Gas Feedstock (Secondary Feedstock) Consumption (Thousand Metric Tons)

Activity	1990		1997	1998	1999	2000	2001	2002	2003
Primary Feedstock	1,864		2,450	2,530	2,563	2,521	2,339	2,398	2,331
Secondary Feedstock	302		378	397	410	415	408	379	388

For the purposes of emissions estimation, 100 percent of the primary carbon black feedstock is assumed to be derived from petroleum refining byproducts. Carbon black feedstock derived from metallurgical (coal) coke production (e.g., creosote oil) is also used for carbon black production; however, no data are available concerning the annual consumption of coal-derived carbon black feedstock. Carbon black feedstock derived from petroleum refining byproducts is assumed to be 89 percent elemental carbon (Srivastava et al. 1999). It is assumed that 100 percent of the tail gas produced from the carbon black production process is combusted and that none of the tail gas is vented to the atmosphere uncontrolled. The furnace black process is assumed to be the only process used for the production of carbon black because of the lack of data concerning the relatively small amount of carbon black produced using the acetylene black and thermal black processes. The carbon black produced from the furnace black process is assumed to be 97 percent elemental carbon (Othmer et al. 1992).

Uncertainty

The CH_4 emission factors used for petrochemical production are based on a limited number of studies. Using plant-specific factors instead of average factors could increase the accuracy of the emission estimates; however, such data were not available. There may also be other significant sources of CH_4 arising from petrochemical production activities that have not been included in these estimates.

The results of the quantitative uncertainty analysis for the CO_2 emissions from carbon black production calculation are based on feedstock consumption, import and export data, and carbon black production data. The composition of carbon black feedstock varies depending upon the specific refinery production process, and therefore the assumption that carbon black feedstock is 89 percent carbon gives rise to uncertainty. Also, no data are available concerning the consumption of coal-derived carbon black feedstock, so CO_2 emissions from the utilization of coal-based feedstock are not included in the emission estimate. In addition, other data sources indicate that the amount of petroleum-based feedstock used in carbon black production may be underreported by the U.S. Census Bureau. Finally, the amount of carbon black produced from the thermal black process and acetylene black process, although estimated to be a small percentage of the total production, is not known. Therefore, there is some uncertainty associated with the assumption that all of the carbon black is produced using the furnace black process.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-48. Petrochemical production CH_4 emissions were estimated to be between 1.4 and 1.6 Tg CO_2 Eq. at the 95 percent confidence level (or in 19 out of 20 Monte Carlo Stochastic Simulations). This indicates a range of approximately 7 percent below to 7 percent above the emission estimate of 1.5 Tg CO_2 Eq. Petrochemical production CO_2 emissions were estimated to be between 2.8 and 3.1 Tg CO_2 Eq. at the 95 percent confidence level (or in 19 out of 20 Monte Carlo Stochastic Simulations). This indicates a range of approximately 10 percent below to 10 percent above the emission estimate of 2.8Tg CO_2 Eq.

Table 4-48: Tier 2 Quantitative Uncertainty Estimates for CH_4 Emissions from Petrochemical Production and CO_2 Emissions from Carbon Black Production (Tg CO_2 Eq. and Percent)

Source	Gas	2003 Emission Estimate (Tg CO_2 Eq.)	Uncertainty Range Relative to Emission Estimate[a] (Tg CO_2 Eq.)	(%)

			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Petrochemical Production	CH_4	1.5	1.4	1.6	-7%	+7%
Petrochemical Production	CO_2	2.8	2.5	3.1	-10%	+10%

[a] Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

Recalculations Discussion

In previous inventories, CO_2 emissions from carbon black production were not calculated and reported separately in the Industrial Processes sector, but were included in the Carbon Stored in Products from Non-Energy Uses of Fossil Fuels in the Energy sector. Although the CH_4 emissions from petrochemical production did not change for 1990 through 2002 compared to the previous Inventory, the addition of CO_2 emissions from carbon black production caused a large increase in petrochemical production emissions for every year of the time series. Overall, the change resulted in an average annual increase of 2.7 Tg CO_2 Eq. (183 percent) in combined CO_2 and CH_4 emissions from petrochemical production for the period 1990 through 2002.

4.12. Silicon Carbide Production (IPCC Source Category 2B4)

Methane is emitted from the production of silicon carbide, a material used as an industrial abrasive. To make silicon carbide (SiC), quartz (SiO_2) is reacted with carbon in the form of petroleum coke. During this reaction, methane is produced from volatile compounds in the petroleum coke. While CO_2 is also emitted from the production process, the requisite data were unavailable for these calculations. CO_2 emissions associated with the use of petroleum coke in the silicon carbide process are accounted for in the Non-energy Uses of Fossil Fuels section in the Energy Chapter. Emissions of CH_4 from silicon carbide production in 2003 were 0.4 Gg CH_4 (0.01 Tg CO_2 Eq.) (see Table 4-49).

Table 4-49: CH_4 Emissions from Silicon Carbide Production (Tg CO_2 Eq. and Gg)

Year	Tg CO_2 Eq.	Gg
1990	+	1
1997	+	1
1998	+	1
1999	+	1
2000	+	1
2001	+	+
2002	+	+
2003	+	+

+ Does not exceed 0.05 Tg CO_2 Eq. or 0.5 Gg

Methodology

Emissions of CH_4 were calculated by multiplying annual silicon carbide production by an emission factor (11.6 kg CH_4/metric ton silicon carbide). This emission factor was derived empirically from measurements taken at Norwegian silicon carbide plants (IPCC/UNEP/OECD/IEA 1997).

Production data for 1990 through 2003 (see Table 4-50) were obtained from the *Minerals Yearbook: Volume I-Metals and Minerals, Manufactured Abrasives* (USGS 1991, 1992, 1993, 1994, 1995, 1996, 1997, 1998, 1999, 2000, 2001, 2002, 2003, 2004).

Table 4-50: Production of Silicon Carbide (Metric Tons)

Year	Metric Tons
1990	105,000
1991	78,900

1992	84,300
1993	74,900
1994	84,700
1995	75,400
1996	73,600
1997	68,200
1998	69,800
1999	65,000
2000	45,000
2001	40,000
2002	30,000
2003	35,000

Uncertainty

The emission factor used for silicon carbide production was based on one study of Norwegian plants. The applicability of this factor to average U.S. practices at silicon carbide plants is uncertain. An alternative would be to calculate emissions based on the quantity of petroleum coke used during the production process rather than on the amount of silicon carbide produced. However, these data were not available.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-51. Silicon carbide production CO_2 emissions were estimated to be between 0.008 and 0.01Tg CO_2 Eq. at the 95 percent confidence level (or in 19 out of 20 Monte Carlo Stochastic Simulations). This indicates a range of approximately 10 percent below to 10 percent above the emission estimate of 0.009 Tg CO_2 Eq.

Table 4-51: Tier 2 Quantitative Uncertainty Estimates for CO_2 Emissions from Silicon Carbide Production (Tg CO_2 Eq. and Percent)

Source	**Gas**	**2003 Emission Estimate (Tg CO_2 Eq.)**	**Uncertainty Range Relative to Emission Estimate[a]**			
			(Tg CO_2 Eq.)		**(%)**	
			Lower Bound	**Upper Bound**	**Lower Bound**	**Upper Bound**
Silicon Carbide Production	CO_2	+	+	+	-10%	+10%

[a] Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.
+ Does not exceed 0.05 Tg CO_2 Eq. or 0.5 Gg.

4.13.Nitric Acid Production (IPCC Source Category 2B2)

Nitric acid (HNO_3) is an inorganic compound used primarily to make synthetic commercial fertilizers. It is also a major component in the production of adipic acid—a feedstock for nylon—and explosives. Virtually all of the nitric acid produced in the United States is manufactured by the catalytic oxidation of ammonia (EPA 1997). During this reaction, N_2O is formed as a by-product and is released from reactor vents into the atmosphere.

Currently, the nitric acid industry controls for NO and NO_2 (i.e., NO_x). As such, the industry uses a combination of non-selective catalytic reduction (NSCR) and selective catalytic reduction (SCR) technologies. In the process of destroying NO_x, NSCR systems are also very effective at destroying N_2O. However, NSCR units are generally not preferred in modern plants because of high energy costs and associated high gas temperatures. NSCRs were widely installed in nitric plants built between 1971 and 1977. Approximately 20 percent of nitric acid plants use NSCR (Choe et al. 1993). The remaining 80 percent use SCR or extended absorption, neither of which is known to reduce N_2O emissions.

Nitrous oxide emissions from this source were estimated to be 15.8 Tg CO_2 Eq. (51.1 Gg) in 2003 (see Table 4-52). Emissions from nitric acid production have decreased by 11 percent since 1990, with the trend in the time series closely tracking the changes in production.

Table 4-52: N_2O Emissions from Nitric Acid Production (Tg CO_2 Eq. and Gg)

Year	Tg CO_2 Eq.	Gg
1990	17.8	58
1997	21.2	68
1998	20.9	67
1999	20.1	65
2000	19.6	63
2001	15.9	51
2002	17.2	56
2003	15.8	51

Methodology

Nitrous oxide emissions were calculated by multiplying nitric acid production by the amount of N_2O emitted per unit of nitric acid produced. The emission factor was determined as a weighted average of 2 kg N_2O / metric ton HNO_3 for plants using non-selective catalytic reduction (NSCR) systems and 9.5 kg N_2O / metric ton HNO_3 for plants not equipped with NSCR (Choe et al. 1993). In the process of destroying NO_x, NSCR systems destroy 80 to 90 percent of the N_2O, which is accounted for in the emission factor of 2 kg N_2O / metric ton HNO_3. An estimated 20 percent of HNO_3 plants in the United States are equipped with NSCR (Choe et al. 1993). Hence, the emission factor is equal to $(9.5 \times 0.80) + (2 \times 0.20) = 8$ kg N_2O per metric ton HNO_3.

Nitric acid production data for 1990 (see Table 4-53) was obtained from *Chemical and Engineering News*, “Facts and Figures” (C&EN 2001). Nitric acid production data for 1991 through 1992 (see Table 4-53) were obtained from *Chemical and Engineering News*, “Facts and Figures” (C&EN 2002). Nitric acid production data for 1993 through 2003 were obtained from *Chemical and Engineering News*, “Facts and Figures” (C&EN 2004). The emission factor range was taken from Choe et al. (1993).

Table 4-53: Nitric Acid Production (Gg)

Year	Gg
1990	7,196
1991	7,191
1992	7,379
1993	7,486
1994	7,904
1995	8,018
1996	8,349
1997	8,556
1998	8,421
1999	8,113
2000	7,898
2001	6,416
2002	6,939
2003	6,388

Uncertainty

The uncertainties contained in these estimates are primarily due to the current organization within the nitric acid industry. A significant degree of uncertainty exists in nitric acid production figures because nitric acid plants are often part of larger production facilities, such as fertilizer or explosives manufacturing. As a result, only a small quantity of nitric acid is sold on the market, making production quantities difficult to track. Emission factors are also difficult to determine because of the large number of plants using a diverse range of technologies.

The results of the Tier 1 quantitative uncertainly analysis are summarized in Table 4-54. Nitric acid production N_2O emissions were estimated to be between 13.2 and 18.5 Tg CO_2 Eq. at the 95 percent confidence level. This indicates a range of 17 percent above to below the 2003 emission estimate of 15.8 Tg CO_2 Eq.

Table 4-54: Tier 1 Quantitative Uncertainty Estimates for N_2O Emissions from Nitric Acid Production (Tg CO_2 Eq. and Percent)

Source	Gas	Year 2003 Emissions (Tg CO_2 Eq.)	Uncertainty (%)	Uncertainty Range Relative to 2003 Emission Estimate (Tg CO_2 Eq.)	
				Lower Bound	**Upper Bound**
Nitric Acid Production	N_2O	15.8	17%	13.2	18.5

Recalculations Discussion

The nitric acid production values for all years 1993 through 2002 were updated using newly published figures (C&EN 2004). Published figures remained consistent for all years of the historical time series except 2002. The updated production data for 2002 resulted in an increase of 0.5 Tg CO_2 Eq. (2.8 percent) in N_2O emissions from nitric acid production for that year.

Planned Improvements

Planned improvements are focused on assessing the plant-by-plant implementation of NO_x abatement technologies to more accurately match plant production capacities to appropriate emission factors, instead of using a national profiling of abatement implementation. Also, any large scale updates to abatement configurations would be useful in revising the national profile.

4.14. Adipic Acid Production (IPCC Source Category 2B3)

Adipic acid production is an anthropogenic source of N_2O emissions. Worldwide, few adipic acid plants exist. The United States is the major producer, with three companies in four locations accounting for approximately one-third of world production. Adipic acid is a white crystalline solid used in the manufacture of synthetic fibers, coatings, plastics, urethane foams, elastomers, and synthetic lubricants. Commercially, it is the most important of the aliphatic dicarboxylic acids, which are used to manufacture polyesters. Approximately 90 percent of all adipic acid produced in the United States is used in the production of nylon 6,6 (CMR 2001). Food grade adipic acid is also used to provide some foods with a “tangy” flavor (Thiemens and Trogler 1991).

Adipic acid is produced through a two-stage process during which N_2O is generated in the second stage. The first stage of manufacturing usually involves the oxidation of cyclohexane to form a cyclohexanone/cyclohexanol mixture. The second stage involves oxidizing this mixture with nitric acid to produce adipic acid. Nitrous oxide is generated as a by-product of the nitric acid oxidation stage and is emitted in the waste gas stream (Thiemens and Trogler 1991). Process emissions from the production of adipic acid vary with the types of technologies and level of emission controls employed by a facility. In 1990, two of the three major adipic acid-producing plants had N_2O abatement technologies in place and, as of 1998, the three major adipic acid production facilities had control systems in place.[13] Only one small plant, representing approximately two percent of production, does not control for N_2O (Reimer 1999).

Nitrous oxide emissions from this adipic acid production were estimated to be 6.0 Tg CO_2 Eq. (19.4 Gg) in 2003 (see Table 4-55).

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[13]During 1997, the N_2O emission controls installed by the third plant operated for approximately a quarter of the year.

Table 4-55: N_2O Emissions from Adipic Acid Production (Tg CO_2 Eq. and Gg)

Year	Tg CO_2 Eq.	Gg
1990	15.2	49
1997	10.3	33
1998	6.0	19
1999	5.5	18
2000	6.0	20
2001	4.9	16
2002	5.9	19
2003	6.0	19

National adipic acid production has increased by approximately 28 percent over the period of 1990 through 2003, to approximately one million metric tons. At the same time, emissions have been significantly reduced due to the widespread installation of pollution control measures.

Methodology

For two production plants, 1990 to 2002 emission estimates were obtained directly from the plant engineer and account for reductions due to control systems in place at these plants during the time series (Childs 2002, 2003). These estimates were based on continuous emissions monitoring equipment installed at the two facilities. Measured estimates for 2003 were unavailable and, thus, were calculated by applying a 1.8 percent production growth rate representative of the industry (see discussion below on sources of production data). For the other two plants, N_2O emissions were calculated by multiplying adipic acid production by an emission factor (i.e., N_2O emitted per unit of adipic acid produced) and adjusting for the actual percentage of N_2O released as a result of plant-specific emission controls. On the basis of experiments, the overall reaction stoichiometry for N_2O production in the preparation of adipic acid was estimated at approximately 0.3 MT of N_2O per MT of product (Thiemens and Trogler 1991). Emissions are estimated using the following equation:

N_2O emissions = [production of adipic acid (MT of adipic acid)] × [0.3 MT N_2O / mt adipic acid] × [1 – (N_2O destruction factor × abatement system utility factor)]

The "N_2O destruction factor" represents the percentage of N_2O emissions that are destroyed by the installed abatement technology. The "abatement system utility factor" represents the percentage of time that the abatement equipment operates during the annual production period. Overall, in the United States, two of the plants employ catalytic destruction, one plant employs thermal destruction, and the smallest plant uses no N_2O abatement equipment. The N_2O abatement system destruction factor is assumed to be 95 percent for catalytic abatement and 98 percent for thermal abatement (Reimer et al. 1999, Reimer 1999). For the one plant that uses thermal destruction and for which no reported plant-specific emissions are available, the abatement system utility factor is assumed to be 98 percent.

In order to calculate emissions for the two plants where direct emissions measurements were not available, plant-specific production data needed to be estimated since it was unavailable due to reasons of confidentiality. In order to calculate plant-specific production for the two plants, national adipic acid production was allocated to the plant level using the ratio of their known plant capacities to total national capacity for all U.S. plants. The estimated plant production for the two plants was then used for calculating emissions as described above.

National adipic acid production data (see Table 4-56) for 1990 through 2002 were obtained from the American Chemistry Council (ACC 2003). Production Data for 2003 were estimated based on an abstract from a Chemical Economics Handbook report entitled "*Adipic Acid*" indicating that production will increase by an annual average of 1.8 percent from year 2002 to 2006. Plant capacity data for 1990 through 1994 were obtained from *Chemical and Engineering News*, "Facts and Figures" and "Production of Top 50 Chemicals" (C&EN 1992, 1993, 1994, 1995). Plant capacity data for 1995 and 1996 were kept the same as 1994 data. The 1997 plant capacity data were taken from *Chemical Market Reporter* "Chemical Profile: Adipic Acid" (CMR 1998). The 1998 plant capacity data for all four plants and 1999 plant capacity data for three of the plants were obtained from *Chemical Week,* Product focus: adipic acid/adiponitrile (CW 1999). Plant capacity data for 2000 for three of the plants were updated using *Chemical Market Reporter*, "Chemical Profile: Adipic Acid" (CMR 2001). For 2001 through 2003, the plant capacities for these three plants were kept the same as the year 2000 capacities. Plant capacity data for 1999 to 2003 for the one remaining plant was kept the same as 1998.

Table 4-56: Adipic Acid Production (Gg)

Year	Gg
1990	735
1991	708
1992	724
1993	769
1994	821
1995	830
1996	839
1997	871
1998	862
1999	907
2000	925
2001	835
2002	921
2003	937

Uncertainty

The emission factor for adipic acid was based on experiments (Thiemens and Trogler 1991) that attempt to replicate the industrial process and, thereby, measure the reaction stoichiometry for N_2O production in the preparation of adipic acid. However, the extent to which the lab results are representative of actual industrial emission rates is not known.

The allocation of national production data for the two facilities where direct emission measurements were unavailable creates a degree of uncertainty in the adipic acid production data as all plants are assumed to operate at equivalent utilization levels as represented by their capacities. Also, plant capacity reference data is inconsistently available from year to year, which can affect the uncertainty of the allocated production through the time series.

A 5 percent uncertainty level was associated with the activity data available for the two plants that reported emissions. For the remaining two plants, a 20 percent uncertainty level was assumed for production. The emission factor uncertainty for each of these two plants was estimated separately to account for the differences in the use of abatement technologies. For the plant that uses no abatement technology, a 10 percent IPCC-default emission factor uncertainty was assumed appropriate. The abatement factor uncertainty used for the second plant was based on a 5 percent IPCC estimate for the N_2O destruction factor and an assumed 5 percent uncertainty in the abatement system utility factor (IPCC 2000). These two estimates result in an overall uncertainty associated with abatement potential of 7 percent. This abatement uncertainty, combined with the 10 percent IPCC default uncertainty value associated with the emissions factor for unabated emissions, results in an overall 12 percent emission factor uncertainty. Combining the reporting plants emissions uncertainty with the activity data uncertainty and the emission factor uncertainty for the remaining two plants yields an overall uncertainty for the inventory estimate equal to 9 percent of 2003 emissions (see Table 4-57).

The results of the Tier 1 quantitative uncertainly analysis are summarized in Table 4-57. Adipic acid production N_2O emissions were estimated to be between 5.5 and 6.5 Tg CO_2 Eq. at the 95 percent confidence level. This indicates a range of 9 percent above to below the 2003 emission estimate of 6.0 Tg CO_2 Eq.

Table 4-57: Tier 1 Quantitative Uncertainty Estimates for N_2O Emissions from Adipic Acid Production (Tg CO_2 Eq. and Percent)

Source	Gas	Year 2003	Uncertainty	Uncertainty Range Relative to

		Emissions (Tg CO_2 Eq.)	(%)	2003 Emission Estimate (Tg CO_2 Eq.)	
				Lower Bound	Upper Bound
Adipic Acid Production	N_2O	6.0	9%	5.5	6.5

QA/QC and Verification

In addition to performing Tier 1 level QA/QC and verification, trends in the production of the synthetic nylon fibers industry were compared to trends in adipic acid production to confirm a reasonable agreement, since almost 90 percent of the adipic acid produced in the United States is used in the production of nylon 6,6.

Planned Improvements

Improvement efforts will be focused on obtaining direct measurement data from the remaining two plants when and if they become available. If they become available, cross verification with top-down approaches will provide a useful Tier 2 level QA check. Also, additional information on the actual performance of the latest catalytic and thermal abatement equipment at plants with continuous emission monitoring may support the re-evaluation of current default abatement values.

4.15. Substitution of Ozone Depleting Substances (IPCC Source Category 2F)

Hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs) are used as alternatives to several classes of ozone-depleting substances (ODSs) that are being phased out under the terms of the *Montreal Protocol* and the Clean Air Act Amendments of 1990.[14] Ozone depleting substances—chlorofluorocarbons (CFCs), halons, carbon tetrachloride, methyl chloroform, and hydrochlorofluorocarbons (HCFCs)—are used in a variety of industrial applications including refrigeration and air conditioning equipment, solvent cleaning, foam production, sterilization, fire extinguishing, and aerosols. Although HFCs and PFCs, are not harmful to the stratospheric ozone layer, they are potent greenhouse gases. Emission estimates for HFCs and PFCs used as substitutes for ODSs are provided in Table 4-58 and Table 4-59.

Table 4-58: Emissions of HFCs and PFCs from ODS Substitution (Tg CO_2 Eq.)

Gas	1990		1997	1998	1999	2000	2001	2002	2003
HFC-23	+		+	+	0.1	0.1	0.1	0.1	0.1
HFC-32	+		0.2	0.3	0.3	0.3	0.3	0.3	0.4
HFC-125	+		7.0	8.8	10.0	11.2	12.3	13.4	14.7
HFC-134a	+		31.4	36.7	42.2	48.0	52.7	56.9	60.5
HFC-143a	+		3.5	5.2	6.6	8.2	10.1	12.2	14.6
HFC-236fa	+		0.1	0.4	0.9	1.4	1.8	2.1	2.3
CF_4	+		+	+	+	+	+	+	+
Others*	0.4		4.2	5.2	5.7	5.9	6.1	6.5	6.9
Total	**0.4**		**46.5**	**56.6**	**65.8**	**75.0**	**83.3**	**91.5**	**99.5**

+ Does not exceed 0.05 Tg CO_2 Eq.
* Others include HFC-152a, HFC-227ea, HFC-245fa, HFC-4310mee, and PFC/PFPEs, the latter being a proxy for a diverse collection of PFCs and perfluoropolyethers (PFPEs) employed for solvent applications. For estimating purposes, the GWP value used for PFC/PFPEs was based upon C_6F_{14}.
Note: Totals may not sum due to independent rounding.

Table 4-59: Emissions of HFCs and PFCs from ODS Substitution (Mg)

[14] [42 U.S.C § 7671, CAA § 601]

Gas	1990		1997	1998	1999	2000	2001	2002	2003
HFC-23	+		3	4	4	5	5	6	6
HFC-32	+		289	430	439	441	459	492	541
HFC-125	+		2,516	3,134	3,571	4,004	4,385	4,777	5,246
HFC-134a	+		24,136	28,202	32,491	36,888	40,512	43,798	46,559
HFC-143a	+		926	1,369	1,738	2,162	2,647	3,203	3,834
HFC-236fa	+		9	64	142	214	281	341	369
CF_4	+		+	1	1	1	1	2	2
Others*	M		M	M	M	M	M	M	M

M (Mixture of Gases)
+ Does not exceed 0.5 Mg
* Others include HFC-152a, HFC-227ea, HFC-245fa, HFC-4310mee and PFC/PFPEs, the latter being a proxy for a diverse collection of PFCs and perfluoropolyethers (PFPEs) employed for solvent applications.

In 1990 and 1991, the only significant emissions of HFCs and PFCs as substitutes to ODSs were relatively small amounts of HFC-152a—a component of the refrigerant blend R-500 used in chillers—and HFC-134a in refrigeration end-uses. Beginning in 1992, HFC-134a was used in growing amounts as a refrigerant in motor vehicle air-conditioners and in refrigerant blends such as R-404A.[15] In 1993, the use of HFCs in foam production and as an aerosol propellant began, and in 1994 these compounds also found applications as solvents and sterilants. In 1995, ODS substitutes for halons entered widespread use in the United States as halon production was phased-out.

The use and subsequent emissions of HFCs and PFCs as ODS substitutes has been increasing from small amounts in 1990 to 99.5 Tg CO_2 Eq. in 2003. This increase was in large part the result of efforts to phase out CFCs and other ODSs in the United States. In the short term, this trend is expected to continue, and will likely accelerate over the next decade as HCFCs, which are interim substitutes in many applications, are themselves phased-out under the provisions of the Copenhagen Amendments to the *Montreal Protocol*. Improvements in the technologies associated with the use of these gases and the introduction of alternative gases and technologies, however, may help to offset this anticipated increase in emissions.

Methodology

A detailed Vintaging Model of ODS-containing equipment and products was used to estimate the actual—versus potential—emissions of various ODS substitutes, including HFCs and PFCs. The name of the model refers to the fact that the model tracks the use and emissions of various compounds for the annual "vintages" of new equipment that enter service in each end-use. This Vintaging Model predicts ODS and ODS substitute use in the United States based on modeled estimates of the quantity of equipment or products sold each year containing these chemicals and the amount of the chemical required to manufacture and/or maintain equipment and products over time. Emissions for each end-use were estimated by applying annual leak rates and release profiles, which account for the lag in emissions from equipment as they leak over time. By aggregating the data for more than 40 different end-uses, the model produces estimates of annual use and emissions of each compound. Further information on the Vintaging Model is contained in Annex 3.8.

Uncertainty

Given that emissions of ODS substitutes occur from thousands of different kinds of equipment and from millions of point and mobile sources throughout the United States, emission estimates must be made using analytical tools such as the Vintaging Model or the methods outlined in IPCC/UNEP/OECD/IEA (1997). Though the model is more comprehensive than the IPCC default methodology, significant uncertainties still exist with regard to the levels of

[15] R-404A contains HFC-125, HFC-143a, and HFC-134a.

equipment sales, equipment characteristics, and end-use emissions profiles that were used to estimate annual emissions for the various compounds.

The Vintaging Model estimates emissions from over 40 end-uses, but the uncertainty estimation was performed on only the top 14 end-uses, which account for 95 percent of emissions from this source category. In order to calculate uncertainty, functional forms were developed to simplify some of the complex "vintaging" aspects of some end-use sectors, especially with respect to refrigeration and air-conditioning, and to a lesser degree, fire extinguishing. These sectors calculate emissions based on the entire lifetime of equipment, not just equipment put into commission in the current year, which necessitated these simplifying equations. The functional forms used variables that included growth rates, emission factors, transition from ODSs, change in charge size as a result of the transition, disposal quantities, disposal emission rates, and either stock for the current year or original ODS consumption. Uncertainty was estimated around each variable within the functional forms based on expert judgment, and a Monte Carlo analysis was performed.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-60. Substitution of ozone depleting substances HFC and PFC emissions were estimated to be between 89.9 and 108.4 Tg CO_2 Eq. at the 95 percent confidence level (or in 19 out of 20 Monte Carlo Stochastic Simulations). This indicates a range of approximately 10 percent below to 10 percent above the emission estimate of 99.5 Tg CO_2 Eq.

Table 4-60: Tier 2 Quantitative Uncertainty Estimates for HFC and PFC Emissions from ODS Substitution (Tg CO_2 Eq. and Percent)

Source	Gases	2003 Emission Estimate (Tg CO_2 Eq.)	Uncertainty Range Relative to Emission Estimate[a] (Tg CO_2 Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Substitution of Ozone Depleting Substances	HFCs and PFCs	99.5	89.9	108.4	-10%	+9%

[a] Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

Recalculations Discussion

An extensive review of the chemical substitution trends, market sizes, growth rates, and charge sizes, together with input from industry representatives, resulted in updated assumptions for the Vintaging Model. These changes resulted in an average annual net increase of less than 0.1 Tg CO_2 Eq. (4.1 percent) in HFC and PFC emissions from the substitution of ozone depleting substances for the period 1990 through 2002.

4.16. HCFC-22 Production (IPCC Source Category 2E1)

Trifluoromethane (HFC-23 or CHF_3) is generated as a by-product during the manufacture of chlorodifluoromethane (HCFC-22), which is primarily employed in refrigeration and air conditioning systems and as a chemical feedstock for manufacturing synthetic polymers. Between 1990 and 2000, U.S. production of HCFC-22 rose significantly as HCFC-22 replaced chlorofluorocarbons (CFCs) in many applications. Since 2000, however, U.S. production has declined to levels near those of the early to mid 1990s. Because HCFC-22 depletes stratospheric ozone, its production for non-feedstock uses is scheduled to be phased out by 2020 under the U.S. Clean Air Act.[16] Feedstock production, however, is permitted to continue indefinitely.

[16] As construed, interpreted, and applied in the terms and conditions of the *Montreal Protocol on Substances that Deplete the Ozone Layer*. [42 U.S.C. §7671m(b), CAA §614]

HCFC-22 is produced by the reaction of chloroform ($CHCl_3$) and hydrogen fluoride (HF) in the presence of a catalyst, $SbCl_5$. The reaction of the catalyst and HF produces $SbCl_xF_y$, (where x + y = 5), which reacts with chlorinated hydrocarbons to replace chlorine atoms with fluorine. The HF and chloroform are introduced by submerged piping into a continuous-flow reactor that contains the catalyst in a hydrocarbon mixture of chloroform and partially fluorinated intermediates. The vapors leaving the reactor contain HCFC-21 ($CHCl_2F$), HCFC-22 ($CHClF_2$), HFC-23 (CHF_3), HCl, chloroform, and HF. The under-fluorinated intermediates (HCFC-21) and chloroform are then condensed and returned to the reactor, along with residual catalyst, to undergo further fluorination. The final vapors leaving the condenser are primarily HCFC-22, HFC-23, HCl and residual HF. The HCl is recovered as a useful byproduct, and the HF is removed. Once separated from HCFC-22, the HFC-23 is generally vented to the atmosphere as an unwanted by-product, or may be captured for use in a limited number of applications.

Emissions of HFC-23 in 2003 were estimated to be 12.3 Tg CO_2 Eq. (1.1 Gg). This quantity represents a 38 percent decline from 2002 emissions and a 65 percent decline from 1990 emissions. Both declines are primarily due to the steady decline in the emission rate of HFC-23 (i.e., the amount of HFC-23 emitted per kilogram of HCFC-22 manufactured). Three HCFC-22 production plants operated in the United States in 2003, two of which used thermal oxidation to significantly lower their HFC-23 emissions.

Table 4-61: HFC-23 Emissions from HCFC-22 Production (Tg CO_2 Eq. and Gg)

Year	Tg CO_2 Eq.	Gg
1990	35.0	3
1997	30.0	3
1998	40.1	3
1999	30.4	3
2000	29.8	3
2001	19.8	2
2002	19.8	2
2003	12.3	1

Methodology

The methodology employed for estimating emissions is based upon measurements at individual HCFC-22 production plants. Plants using thermal oxidation to abate their HFC-23 emissions monitor the performance of their oxidizers to verify that the HFC-23 is almost completely destroyed. The other plants periodically measure HFC-23 concentrations in the output stream using gas chromatography. This information is combined with information on quantities of critical feed components (e.g., HF) and/or products (HCFC-22) to estimate HFC-23 emissions using a material balance approach. HFC-23 concentrations are determined at the point the gas leaves the chemical reactor; therefore, estimates also include fugitive emissions.

Production data and emission estimates were prepared in cooperation with the U.S. manufacturers of HCFC-22 (ARAP 1997, 1999, 2000, 2001, 2002, 2003, 2004; RTI 1997). Annual estimates of U.S. HCFC-22 production are presented in Table 4-62.

Table 4-62: HCFC-22 Production (Gg)

Year	Gg
1990	138.9
1991	142.7
1992	149.6
1993	132.4
1994	146.8
1995	154.7
1996	166.1
1997	164.5
1998	182.8

1999	165.5
2000	186.9
2001	152.4
2002	144.2
2003	138.0

Uncertainty

A high level of confidence has been attributed to the HFC-23 concentration data employed because measurements were conducted frequently and accounted for day-to-day and process variability. The results of the Tier 1 quantitative uncertainly analysis are summarized in Table 4-63. HCFC-22 production HFC-23 emissions were estimated to be between 11.1 and 13.6 Tg CO_2 Eq. at the 95 percent confidence level. This indicates a range of 10 percent above and below the 2003 emission estimate of 12.3 Tg CO_2 Eq.

Table 4-63: Tier 1 Quantitative Uncertainty Estimates for HFC-23 Emissions from HCFC-22 Production (Tg CO_2 Eq. and Percent)

Source	**Gas**	**Year 2003 Emissions (Tg CO_2 Eq.)**	**Uncertainty (%)**	**Uncertainty Range Relative to 2003 Emission Estimate (Tg CO_2 Eq.)**	
				Lower Bound	**Upper Bound**
HCFC-22 Production	HFC-23	12.3	10%	11.1	13.6

Recalculations Discussion

The historical time series was adjusted to fully reflect reports from the Alliance for Responsible Atmospheric Policy. These changes resulted in an average annual decrease of less than 0.1 Tg CO_2 Eq. (0.01 percent) in HFC emissions from HCFC-22 through the period 1990 through 2002.

4.17. Electrical Transmission and Distribution (IPCC Source Category 2F7)

The largest use of SF_6, both in the United States and internationally, is as an electrical insulator and interrupter in equipment that transmits and distributes electricity (RAND 2002). The gas has been employed by the electric power industry in the United States since the 1950s because of its dielectric strength and arc-quenching characteristics. It is used in gas-insulated substations, circuit breakers, and other switchgear. Sulfur hexafluoride has replaced flammable insulating oils in many applications and allows for more compact substations in dense urban areas.

Fugitive emissions of SF_6 can escape from gas-insulated substations and switch gear through seals, especially from older equipment. The gas can also be released during equipment manufacturing, installation, servicing, and disposal. Emissions of SF_6 from electrical transmission and distribution systems were estimated to be 14.1 Tg CO_2 Eq. (0.6 Gg) in 2003. This quantity represents a 52 percent decrease from the estimate for 1990 (see Table 4-64 and Table 4-65). This decrease, which is reflected in the atmospheric record (Maiss and Brenninkmeijer 2000), is believed to be a response to increases in the price of SF_6 during the 1990s and to growing awareness of the environmental impact of SF_6 emissions, through programs such as the EPA's SF_6 Emission Reduction Partnership for Electric Power Systems.

Table 4-64: SF_6 Emissions from Electric Power Systems and Original Equipment Manufactures (Tg CO_2 Eq.)

Year	**Electric Power Systems**	**Original Equipment Manufacturers**	**Total**
1990	28.9	0.3	**29.2**
1997	21.3	0.3	**21.7**
1998	16.7	0.4	**17.1**
1999	15.8	0.6	**16.4**

2000	15.0	0.7	**15.6**
2001	14.7	0.7	**15.4**
2002	14.0	0.7	**14.7**
2003	13.4	0.7	**14.1**

Table 4-65: SF_6 Emissions from Electric Power Systems and Original Equipment Manufacturers (Gg)

Year	Emissions
1990	1.2
1997	0.9
1998	0.7
1999	0.7
2000	0.7
2001	0.6
2002	0.6
2003	0.6

Methodology

The estimates of emissions from electric transmission and distribution are comprised of emissions from electric power systems and emissions from the manufacture of electrical equipment. The methodologies for estimating both sets of emissions are described below.

1999 to 2003 Emissions from Electric Power Systems

Emissions from electric power systems from 1999 to 2003 were estimated based on (1) reporting from utilities participating in EPA's SF_6 Emissions Reduction Partnership for Electric Power Systems, which began in 1999, and (2) utilities' transmission miles as reported in the 2001 and 2004 Utility Data Institute (UDI) Directories of Electric Power Producers and Distributors (UDI 2001, 2004). (Transmission miles are defined as the miles of lines carrying voltages above 34.5 kV.) Between 1999 and 2003, participating utilities represented between 31 percent and 35 percent of total U.S. transmission miles. The emissions reported by participating utilities each year were added to the emissions estimated for non-reporting utilities in that year. Emissions from non-reporting utilities were estimated using the results of a regression analysis that showed that the emissions of reporting utilities were most strongly correlated with their transmission miles. As described further below, the transmission miles of the various types of non-reporting utilities were multiplied by the appropriate regression coefficients, yielding an estimate of emissions. Transmission miles are clearly physically related to emissions, since in the United States, SF_6 is contained primarily in transmission equipment rated at or above 34.5 kV.

The regression equations reflect two distinctions among non-reporting utilities: (1) between small and large utilities (i.e., with less or more than 10,000 transmission miles, respectively), and (2) between utilities that do not participate in the SF_6 Emission Reduction Partnership (non-partners) and those that participate but that have not reported in a given year (non-reporting partners). (Historically, these non-reporting partners have accounted for 5 percent or less of total estimated partner emissions.) The distinction between small and large utilities was made because the regression analysis showed that the relationship between emissions and transmission miles differed for small and large facilities. The distinction between non-partners and non-reporting partners was made because the emission trends of these two groups were believed to be different. Reporting partners have reduced their emission rates significantly since 1999. The emission trend of non-reporting partners was believed to be similar to that of the reporting partners, because all partners commit to reducing SF_6 emissions through technically and economically feasible means. However, non-partners were assumed not to have implemented any changes that would have reduced emissions over time.

To estimate emissions from non-partners in every year since 1999, the following regression equations were used. These equations were developed based on the 1999 SF_6 emissions reported by 49 partner utilities (representing approximately 31 percent of U.S. transmission miles), and 2000 transmission mileage data obtained from the 2001 UDI Directory of Electric Power Producers and Distributors (UDI 2001):

Non-partner small utilities (less than 10,000 transmission miles, in kilograms):

$$\text{Emissions} = 0.874 \times \text{Transmission Miles}$$

Non-partner large utilities (more than 10,000 transmission miles, in kilograms):

$$\text{Emissions} = 0.558 \times \text{Transmission Miles}$$

To estimate emissions from non-reporting partners in each year, the regression equations based on the emissions reported by partners in that year were used. To estimate non-reporting partner emissions in 2003, the regression equations were based on the 2003 SF_6 emissions reported by 51 partner utilities, and updated 2003 transmission mileage data obtained from the 2004 UDI Directory of Electric Power Producers and Distributors (UDI 2004). The resulting equations for 2003 are:

Non-reporting partner small utilities (less than 10,000 transmission miles, 2003, in kilograms):

$$\text{Emissions} = 0.398 \times \text{Transmission Miles}$$

Non-reporting partner large utilities (more than 10,000 transmission miles, 2003, in kilograms):

$$\text{Emissions} = 0.387 \times \text{Transmission Miles}$$

As indicated from the 2001 and 2004 UDI Directories of Electric Power Producers and Distributors (UDI 2001, 2004), the U.S. transmission system has grown by over 14,000 miles between 2000 and 2003. To reflect the fact that this increase probably occurred gradually, transmission mileage was assumed to increase exponentially at an annual rate of approximately 0.7 percent during the 2000 to 2003 time period.

For each year, total emissions were then determined by summing the partner-reported emissions, the non-reporting partner emissions (determined with that year's regression equation for the partners), and the non-partner emissions (determined using the 1999 regression equation).

1990 to 1998 Emissions from Manufacture of Electric Equipment

Because most participating utilities reported emissions only for 1999 through 2003, modeling SF_6 emissions from electric power systems for the years 1990 through 1998 was necessary. To do so, it was assumed that during this period, U.S. emissions followed the same trajectory as global emissions from this source. To estimate global emissions, the RAND survey of global SF_6 sales to electric utilities was used, together with the following equation, which is derived from the equation for emissions in the IPCC report, *Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories* (IPCC 2001):

$$\text{Emissions (kilograms)} = SF_6 \text{ purchased to refill existing equipment (kilograms)} + \text{nameplate capacity of retiring equipment (kilograms)}$$

Note that the above equation holds whether the gas from retiring equipment is released or recaptured; if the gas is recaptured, it is used to refill existing equipment, lowering the amount of SF_6 purchased by utilities for this purpose.

Sulfur hexaflouride purchased to refill existing equipment in a given year was assumed to be approximately equal to the SF_6 purchased by utilities in that year. Gas purchases by utilities and equipment manufacturers from 1961 through 2001 are available from the RAND (2002) survey. To estimate the quantity of SF_6 released from retiring equipment, the nameplate capacity of retiring equipment in a given year was assumed to equal 77.5 percent of the amount of gas purchased by electrical equipment manufacturers 30 years previous (e.g., in 1990, the nameplate capacity of retiring equipment was assumed to equal 77.5 percent of the gas purchased in 1960). The remaining 22.5 percent was assumed to have been emitted at the time of manufacture. The 22.5 percent emission rate is an average of IPCC SF_6 emission rates for Europe and Japan for years before 1996 (IPCC 2001). The 30-year lifetime for electrical equipment is also drawn from IPCC (2001). The results of the two components of the above equation were then summed to yield estimates of global SF_6 emissions from 1990 through 1998.

To estimate U.S. emissions for 1990 through 1998, estimated global emissions for each year from 1990 through 1998 were divided by the estimated global emissions from 1999. The result was a time series of factors that express each year's global emissions as a multiple of 1999 global emissions. To estimate historical U.S. emissions, the factor for each year was multiplied by the estimated U.S. emissions of SF_6 from electric power systems in 1999 (estimated to be 15.8 Tg CO_2 Eq.).

1990 to 2003 Emissions from Manufacture of Electrical Equipment

The 1990 to 2003 emissions estimates for original equipment manufacturers (OEMs) were derived by assuming that manufacturing emissions equal 10 percent of the quantity of SF_6 charged into new equipment. The quantity of SF_6 charged into new equipment was estimated based on statistics compiled by the National Electrical Manufacturers Association (NEMA). These statistics were provided for 1990 to 2000; the quantities of SF_6 charged into new equipment for 2001 to 2003 were assumed to equal that charged into equipment in 2000. The 10 percent emission rate is the average of the "ideal" and "realistic" manufacturing emission rates (4 percent and 17 percent, respectively) identified in a paper prepared under the auspices of the International Council on Large Electric Systems (CIGRE) in February 2002 (O'Connell et al. 2002).

Uncertainty

For electric power systems, individual partner-reported SF_6 data was assumed to have an uncertainty of 10 percent. This uncertainty was assumed to incorporate potential errors associated with the weighing of SF_6 cylinders and the tracking of SF_6 purchases and use. Using error propagation, the cumulative uncertainty of all partner-reported data was estimated to be 5 percent.

There are two sources of uncertainty associated with the regression equations used to extrapolate U.S. emissions from participant reports: 1) uncertainty in the coefficients (as defined by the regression standard error estimate); and 2) the uncertainty in total transmission miles for non-partners and non-reporting partners, which is assumed to be 10 percent. In addition, there is also uncertainty in the basic assumption that all non-reporting partners will follow the trend defined by reporting partners in a specific year, as well as uncertainty that the emission factor used for utilities that were not participants, which accounted for approximately 65 percent of U.S. transmission miles, will remain at levels defined by partners who reported in 1999. However, neither of these uncertainties was modeled.

For OEMs, uncertainty estimates are based on the assumption that SF_6 statistics obtained from NEMA have an uncertainty of 10 percent. Additionally, the OEMs SF_6 emissions rate has an uncertainty bounded by the proposed "actual" and "ideal" emission rates defined in O'Connell, et al. (2002). That is, the uncertainty in the emission rate is approximately 65 percent.

A Monte Carlo analysis was applied to estimate the overall uncertainty of the emission estimate for SF_6 from electrical transmission and distribution. For each defined parameter (i.e., equation coefficient, transmission mileage, and partner-specific SF_6 emissions data for electric power systems; and SF_6 emission rate and statistics for OEMs), random variables were selected from probability density functions, all assumed to have normal distributions about the mean. The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-67. Electrical Transmission and Distribution SF_6 emissions were estimated to be between 12.3 and 16.1 Tg CO_2 Eq. at the 95 percent confidence level (or in 19 out of 20 Monte Carlo Stochastic Simulations). This indicates a range of approximately 13 percent below and 14 percent above the emission estimate of 14.1 Tg CO_2 Eq.

Table 4-66: Simulated Variables for Tier 2 Uncertainty Analysis

Parameter	Probability Distribution	Uncertainty[a] (%)
Total Partner-Reported SF_6 Data (kg SF_6)	Normal	5
Coefficient – Small Utilities, Non-Partners	Normal	11
Coefficient – Large Utilities, Non-Partners	Normal	21
Coefficient – Small Utilities, Non-Reporting Partners	Normal	21
Coefficient – Large Utilities, Non-Reporting Partners	Normal	NA[b]
Transmission Miles – Small Utilities, Non-Partners	Normal	10

Transmission Miles – Large Utilities, Non-Partners	Normal	10
Transmission Miles – Small Utilities, Non-Reporting Partners	Normal	10
Transmission Miles – Large Utilities, Non-Reporting Partner	Normal	NA[b]
OEM SF_6 Emission Rate (percent)	Normal	65
SF_6 Charged to Equipment (kg SF_6)	Normal	10

[a] Reflects a 95 percent confidence interval.
[b] Not applicable. In 2003, all large utility partners reported to the SF_6 Emission Reduction Partnership.

Table 4-67: Tier 2 Quantitative Uncertainty Estimates for SF_6 Emissions from Electrical Transmission and Distribution (Tg CO_2 Eq. and Percent)

Source	Gas	2003 Emission Estimate (Tg CO_2 Eq.)	Uncertainty Range Relative to 2003 Emission Estimate[a] (Tg CO_2 Eq.)		Uncertainty Range Relative to 2003 Emission Estimate[a] (%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Electrical Transmission and Distribution	SF_6	14.1	12.3	16.1	-13%	+14%

[a] Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

Recalculations Discussion

Electric power system emission estimates for the years 2000, 2001 and 2002 were recalculated based on a combination of additional historical partner data and the incorporation of more up-to-date transmission mileage data. For historical partner submissions, the regression equations for each respective year were updated and new extrapolations to non-reporting partners were made. Additionally, recalculations were conducted using updated transmission mileage data, which reflect the growth of the U.S. transmission system. Previously-reported 2001 and 2002 emission estimates had utilized the 2001 UDI Directory of Electric Power Producers and Distributors (UDI 2001) for transmission mileage data (i.e., 2000 data). As mentioned above, transmission mileage data for 2001 and 2002 were adjusted to account for increases in transmission mileage during this period. These adjustments have been incorporated in non-reporting partner regression equation re-calculations, resulting in revised estimates of non-partner and non-reporting partner emissions. The combination of these changes resulted in an average annual decrease of less than 0.1 Tg CO_2 Eq. (0.2 percent) in SF_6 emissions from electrical transmission and distribution for the period 2000 through 2002.

4.18. Aluminum Production (IPCC Source Category 2C3)

Aluminum is a light-weight, malleable, and corrosion-resistant metal that is used in many manufactured products, including aircraft, automobiles, bicycles, and kitchen utensils. In 2003, the United States was the third largest producer of primary aluminum, with 10 percent of the world total (USGS 2004). The United States was also a major importer of primary aluminum. The production of primary aluminum—in addition to consuming large quantities of electricity—results in process-related emissions of CO_2 and two perfluorocarbons (PFCs): perfluoromethane (CF_4) and perfluoroethane (C_2F_6).

Carbon dioxide is emitted during the aluminum smelting process when alumina (aluminum oxide, Al_2O_3) is reduced to aluminum using the Hall-Heroult reduction process. The reduction of the alumina occurs through electrolysis in a molten bath of natural or synthetic cryolite (Na_3AlF_6). The reduction cells contain a carbon lining that serves as the cathode. Carbon is also contained in the anode, which can be a carbon mass of paste, coke briquettes, or prebaked carbon blocks from petroleum coke. During reduction, most of this carbon is oxidized and released to the atmosphere as CO_2.

Process emissions of CO_2 from aluminum production were estimated to be 4.2 Tg CO_2 Eq. (4,219 Gg) in 2003 (see Table 4-68). The carbon anodes consumed during aluminum production consist of petroleum coke and, to a minor extent, coal tar pitch. The petroleum coke portion of the total CO_2 process emissions from aluminum production is considered to be a non-energy use of petroleum coke, and is accounted for here and not under the CO_2 from Fossil Fuel Combustion source category of the Energy sector. Similarly, the coal tar pitch portion of these CO_2 process emissions is accounted for here rather than in the Iron and Steel source category of the Industrial Processes sector.

Table 4-68: CO_2 Emissions from Aluminum Production (Tg CO_2 Eq. and Gg)

Year	Tg CO_2 Eq.	Gg
1990	6.3	6,315
1997	5.6	5,621
1998	5.8	5,792
1999	5.9	5,895
2000	5.7	5,723
2001	4.1	4,114
2002	4.2	4,220
2003	4.2	4,219

In addition to CO_2 emissions, the aluminum production industry is also a source of PFC emissions. During the smelting process, when the alumina ore content of the electrolytic bath falls below critical levels required for electrolysis, rapid voltage increases occur, termed "anode effects." These anode effects cause carbon from the anode and fluorine from the dissociated molten cryolite bath to combine, thereby producing fugitive emissions of CF_4 and C_2F_6. In general, the magnitude of emissions for a given level of production depends on the frequency and duration of these anode effects. As the frequency and duration of the anode effects increase, a corresponding rise in emission levels occurs.

Emissions of PFCs from primary aluminum production are estimated to have declined 79 percent since 1990. Since 1990, emissions of CF_4 and C_2F_6 have declined 80 percent and 77 percent, respectively, to 3.3 Tg CO_2 Eq. of CF_4 (0.5 Gg) and 0.5 Tg CO_2 Eq. of C_2F_6 (0.1 Gg) in 2003, as shown in Table 4-69 and Table 4-70. This decline was due both to reductions in domestic aluminum production and to actions taken by aluminum smelting companies to reduce the frequency and duration of anode effects.

Table 4-69: PFC Emissions from Aluminum Production (Tg CO_2 Eq.)

Year	CF_4	C_2F_6	Total
1990	16.1	2.3	18.3
1997	9.8	1.2	11.0
1998	8.1	1.0	9.1
1999	8.0	0.9	9.0
2000	8.1	0.9	9.0
2001	3.5	0.5	4.0
2002	4.5	0.7	5.2
2003	3.3	0.5	3.8

Note: Totals may not sum due to independent rounding.

Table 4-70: PFC Emissions from Aluminum Production (Gg)

Year	CF_4	C_2F_6
1990	2.5	0.2
1997	1.5	0.1
1998	1.2	0.1
1999	1.2	0.1
2000	1.2	0.1
2001	0.5	0.1
2002	0.7	0.1
2003	0.5	0.1

U.S. primary aluminum production for 2003—totaling 2.7 million metric tons—remained similar to 2002 production levels. Due to high electric power costs in various regions of the country, aluminum production has been curtailed at several U.S. smelters, which resulted in current production levels that were nearly 26 percent lower than 2000 levels in 2003. The transportation industry remained the largest domestic consumer of primary aluminum, accounting for about 35 percent of U.S. consumption (USGS 2004).

Methodology

Carbon dioxide is generated during alumina reduction to aluminum metal following the reaction below:

$$2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2$$

The CO_2 emission factor employed was estimated from the production of primary aluminum metal and the carbon consumed by the process. Emissions vary depending on the specific technology used by each plant (e.g., Prebake or Soderberg). The *Revised 1996 IPCC Guidelines* (IPCC/UNEP/OECD/IEA 1997) provide CO_2 emission factors for each technology type. During alumina reduction in a prebake anode cell process, approximately 1.5 metric tons of CO_2 are emitted for each metric ton of aluminum produced (IPCC/UNEP/OECD/IEA 1997). Similarly, during alumina reduction in a Soderberg cell process, approximately 1.8 metric tons of CO_2 are emitted per metric ton of aluminum produced (IPCC/UNEP/OECD/IEA 1997). Based on information gathered by EPA's Voluntary Aluminum Industrial Partnership (VAIP) program, production was assumed to be split 80 percent prebake and 20 percent Soderberg for the whole time series.

PFC emissions from aluminum production were estimated using a per-unit production emission factor that is expressed as a function of operating parameters (anode effect frequency and duration), as follows:

$$\text{PFC } (CF_4 \text{ or } C_2F_6) \text{ kg/metric ton Al} = S \times \text{Anode Effect Minutes/Cell-Day}$$

where,

S = Slope coefficient (kg PFC/metric ton Al/(Anode Effect minutes/cell day))
Anode Effect Minutes/Cell-Day = Anode Effect Frequency/Cell-Day × Anode Effect Duration (minutes)

Smelter-specific slope coefficients that are based on field measurements yield the most accurate results. To estimate emissions between 1990 and 2002, smelter-specific coefficients were available and were used for 12 out of the 23 U.S. smelters. To estimate 2003 emissions, smelter-specific coefficients were available and were used for 6 out of the 17 operating U.S. smelters. For the remaining 11 operating smelters, technology-specific slope coefficients from *Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories* (IPCC 2001) were applied. The slope coefficients were combined with smelter-specific anode effect data, collected by aluminum companies and reported to the VAIP, to estimate emission factors over time. In 2003, smelter-specific anode effect data was available for 15 of the 17 operating smelters. Where smelter-specific anode effect data were not available (i.e., 2 out of 17 smelters in 2003, 2 out of 23 smelters between 1990 and 2002), industry averages were used. For all smelters, emission factors were multiplied by annual production to estimate annual emissions at the smelter level. In 2003, smelter-specific production data was available for 16 of the 17 operating smelters; production at the one remaining smelter was estimated based on national aluminum production and capacity data (USGS). Between 1990 and 2003, production data has been provided by 21 of the 23 U.S. smelters. Emissions were then aggregated across smelters to estimate national emissions. The methodology used to estimate emissions is consistent with the methodologies recommended by the *Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories* (IPCC 2001).

National primary aluminum production data for 1990 through 2001 (see Table 4-71) were obtained from USGS, *Mineral Industry Surveys: Aluminum Annual Report* (USGS 1995, 1998, 2000, 2001, 2002). For 2002 and 2003, national aluminum production data were obtained from the United States Aluminum Association's *Primary*

Aluminum Statistics (USAA 2004). The CO_2 emission factors were taken from the *Revised 1996 IPCC Guidelines* (IPCC/UNEP/OECD/IEA 1997).

Table 4-71: Production of Primary Aluminum (Gg)

Year	Gg
1990	4,048
1991	4,121
1992	4,042
1993	3,695
1994	3,299
1995	3,375
1996	3,577
1997	3,603
1998	3,713
1999	3,779
2000	3,668
2001	2,637
2002	2,705
2003	2,705

Uncertainty

The overall uncertainty associated with the 2003 CO_2, CF_4, and C_2F_6 emission estimates were calculated using the IPCC Good Practice Guidance Tier 2 methodology. Uncertainty associated with the parameters used to estimate CO_2 emissions included that associated with production data, with the share of U.S. aluminum production attributable to each smelter type, and with the emission factors applied to production data to calculate emissions. Uncertainty surrounding production data was assumed to be characterized as described below, and other variables were modeled assuming triangular distributions. Emission factors were determined through expert elicitation to be 50 percent certain at a 95 percent confidence level, while the share of production attributed to smelter types were determined to be associated with a 25 percent uncertainty. A Monte Carlo analysis was applied to estimate the overall uncertainty of the emissions estimate for the U.S. aluminum industry as a whole and the results are provided below.

In determining uncertainty associated with emissions of CF_4 and C_2F_6, for each smelter, uncertainty associated with the quantity of aluminum produced and the frequency and duration of anode effects was estimated. A Monte Carlo analysis was then applied to estimate the overall uncertainty of the emissions estimate for each smelter and for the U.S. aluminum industry as a whole. Data on anode effect frequency and duration and production data are assumed to be characterized by a normal distribution. The uncertainty of aluminum production estimates was assumed to be 1 percent or 25 percent, depending on whether a smelter's production was reported or estimated. The uncertainty of the anode effect frequency was assumed to be 2 percent if the data was reported; however, if the data was estimated, the uncertainty ranged from 33 to 78 percent, depending on the smelter technology type. Similarly, the uncertainty in anode effect duration was assumed to be 5 percent for data that was reported, but between 28 and 70 percent for data that was estimated. The uncertainty ranges for estimated technology-specific anode effect frequency and duration are based on the standard deviation of reported anode-effect frequency and duration in the International Aluminum Institute's anode effect survey (IAI 2000).

Additionally, for CF_4 and C_2F_6 emission estimates, uncertainties associated with slope coefficients were calculated. Data for the slope coefficients are assumed to be characterized by a normal distribution. For the three smelters that participated in the 2003 EPA-funded measurement study, CF_4 and C_2F_6 slope coefficient uncertainties were calculated to be 10 percent. For the remaining smelters, given the limited uncertainty data on site-specific slope coefficients (i.e., those developed using IPCC Tier 3b methodology), the overall uncertainty associated with the slope coefficients is conservatively assumed to be similar to that given by the IPCC guidance for technology-specific slope coefficients. Consequently, the uncertainty assigned to the slope coefficients ranged between 10 percent and 35 percent, depending upon the gas and the smelter technology type. In general, where precise quantitative information was not available on the uncertainty of a parameter, a conservative (upper-bound) value was used.

The results of this Tier 2 quantitative uncertainty analysis are summarized in Table 4-72. Aluminum production CO_2 emissions were estimated to be between 2.8 and 5.9 Tg CO_2 Eq. at the 95 percent confidence level (or in 19 out of 20 Monte Carlo Stochastic Simulations). This indicates a range of approximately 34 percent below to 40 percent above the emission estimate of 4.2 Tg CO_2 Eq. Also at the 95 percent confidence interval, aluminum production CF_4 emissions were estimated to be between 2.9 and 3.7 Tg CO_2 Eq. at the 95 percent confidence level. This indicates a range of approximately 11 percent below to 11 percent above the emission estimate of 3.3 Tg CO_2 Eq. Finally aluminum production C_2F_6 emissions were estimated to be between 0.46 and 0.59 Tg CO_2 Eq. at the 95 percent confidence level. This indicates a range of approximately 12 percent below to 13 percent above the emission estimate of 0.5 Tg CO_2 Eq.

Table 4-72: Tier 2 Quantitative Uncertainty Estimates for PFC Emissions from Aluminum Production (Tg CO_2 Eq. and Percent)

Source	Gas	2003 Emission Estimate (Tg CO_2 Eq.)	Uncertainty Range Relative to 2003 Emission Estimate[a]			
			(Tg CO_2 Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Aluminum Production	CO_2	4.2	2.8	5.9	-34%	+40%
Aluminum Production	CF_4	3.3	2.9	3.7	-11%	+11%
Aluminum Production	C_2F_6	0.5	0.5	0.6	-12%	+13%

[a] Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

Occasionally, SF_6 may be used by the aluminum industry as a cover gas or a fluxing and degassing agent in experimental and specialized casting operations. In its application as a cover gas, SF_6 is mixed with nitrogen or CO_2 and injected above the surface of molten aluminum. As a fluxing and degassing agent, SF_6 is mixed with argon, nitrogen, and/or chlorine and blown through molten aluminum. These practices are not employed extensively by primary aluminum producers and are generally isolated to secondary casting firms. The aluminum industry in the United States and Canada has been estimated to use 230 metric tons of SF_6 per year (Maiss and Brenninkmeijer 1998); however, this estimate is highly uncertain.

Historically, SF_6 from aluminum activities has been omitted from estimates of global SF_6 emissions, with the explanation that any emissions would be insignificant (Ko et al. 1993, Victor and MacDonald 1998). Emissions are considered to be insignificant, given that the concentration of SF_6 in the mixtures is small and a portion of the SF_6 is decomposed in the process (MacNeal et al. 1990, Gariepy and Dube 1992, Ko et al. 1993, Ten Eyck and Lukens 1996, Zurecki 1996).

Emissions of SF_6 from aluminum fluxing and degassing have not been estimated. Uncertainties exist as to the quantity of SF_6 used by the aluminum industry and its rate of destruction in its uses as a degassing agent or cover gas.

Recalculations Discussion

The smelter-specific emission factors used for estimating PFC emissions, as well as aluminum production levels, were revised to reflect recently-reported data concerning smelter operating parameters, as well as measurements conducted at three U.S. aluminum smelters. The measurements were part of an EPA-funded study to determine facility-specific slope coefficients. Consequently, these coefficients were used instead of IPCC defaults to calculate smelter-specific emission factors. These data were provided in cooperation with participants in the VAIP program. The combination of these changes resulted in an average annual increase of less than 0.1 Tg CO_2 Eq. (0.2 percent) in PFC emissions from aluminum production for the period 1990 through 2002.

Carbon dioxide emission estimates from aluminum production for 2002 were updated to include aluminum production data from the USAA. Previous CO_2 emission estimates for 2002 were based on aluminum production data from the USGS. This change resulted in a decrease in CO_2 emissions from aluminum production of less than 0.1 Tg CO_2 Eq. (less than -0.1 percent) for 2002.

4.19. Semiconductor Manufacture (IPCC Source Category 2F6)

The semiconductor industry uses multiple long-lived fluorinated gases in plasma etching and plasma enhanced chemical vapor deposition (PECVD) processes to produce semiconductor products. The gases most commonly employed are trifluoromethane (HFC-23 or CHF_3), perfluoromethane (CF_4), perfluoroethane (C_2F_6), nitrogen trifluoride (NF_3), and sulfur hexafluoride (SF_6), although other compounds such as perfluoropropane (C_3F_8) and perfluorocyclobutane (c-C_4F_8) are also used. The exact combination of compounds is specific to the process employed.

A single 300 mm silicon wafer that yields between 400 to 500 semiconductor products (devices or chips) may require as many as 100 distinct fluorinated-gas-using process steps, principally to deposit and pattern dielectric films. Plasma etching (or patterning) of dielectric films, such as silicon dioxide and silicon nitride, is performed to provide pathways for conducting material to connect individual circuit components in each device. The patterning process uses plasma-generated fluorine atoms, which chemically react with exposed dielectric film, to selectively remove the desired portions of the film. The material removed as well as undissociated fluorinated gases flow into waste streams and, unless emission abatement systems are employed, into the atmosphere. PECVD chambers, used for depositing dielectric films, are cleaned periodically using fluorinated and other gases. During the cleaning cycle the gas is converted to fluorine atoms in a plasma, which etches away residual material from chamber walls, electrodes, and chamber hardware. Undissociated fluorinated gases and other products pass from the chamber to waste streams and, unless abatement systems are employed, into the atmosphere. In addition to emissions of unreacted gases, some fluorinated compounds can also be transformed in the plasma processes into different fluorinated compounds which are then exhausted, unless abated, into the atmosphere. For example, when C_2F_6 is used in cleaning or etching, CF_4 is generated and emitted as a process by-product. Besides dielectric film etching and PECVD chamber cleaning, much smaller quantities of fluorinated gases are used to etch polysilicon films and refractory metal films like tungsten.

For 2003, total weighted emissions of all fluorinated greenhouse gases by the U.S. semiconductor industry were estimated to be 4.3 Tg CO_2 Eq. Combined emissions of all fluorinated greenhouse gases are presented in Table 4-73 and Table 4-74 below. The rapid growth of this industry and the increasing complexity of semiconductor products which use more PFCs in the production process have led to an increase in emissions of 48 percent since 1990. The emissions growth rate began to slow after 1997, and emissions declined by 40 percent between 1999 and 2003. This decline is due both to a drop in production (with a continuing decline in silicon consumption) and to the initial implementation of PFC emission reduction methods such as process optimization.

Table 4-73: PFC, HFC, and SF_6 Emissions from Semiconductor Manufacture (Tg CO_2 Eq.)

Year	1990		1997	1998	1999	2000	2001	2002	2003
CF_4	0.7		1.6	1.8	1.8	1.8	1.3	1.1	1.0
C_2F_6	1.5		3.2	3.6	3.7	3.0	2.1	2.2	2.1
C_3F_8	0.0		0.0	0.0	0.0	0.1	0.1	0.1	0.1
C_4F_8	0.0		0.0	0.0	0.0	0.0	0.0	0.0	0.1
HFC-23	0.2		0.4	0.4	0.4	0.3	0.2	0.2	0.2
SF_6	0.5		1.1	1.3	1.3	1.1	0.8	0.7	0.8
NF_3*	0.0		0.1	0.1	0.1	0.1	0.1	0.3	0.2
Total	**2.9**		**6.3**	**7.1**	**7.2**	**6.3**	**4.5**	**4.4**	**4.3**

Note: Totals may not sum due to independent rounding.
* NF_3 emissions are presented for informational purposes, using a GWP of 8,000, and are not included in totals.

Table 4-74: PFC, HFC, and SF_6 Emissions from Semiconductor Manufacture (Mg)

Year	1990		1997	1998	1999	2000	2001	2002	2003

CF_4	115		245	277	281	281	202	175	161
C_2F_6	160		347	391	397	324	231	244	228
C_3F_8	0		0	0	0	17	14	9	13
C_4F_8	0		0	0	0	0	0	5	8
HFC-23	15		33	37	37	23	16	15	17
SF_6	22		48	54	55	46	31	28	35
NF_3	3		8	9	9	11	12	32	30

Methodology

Emissions from semiconductor manufacturing were estimated using three distinct methods, one each for the periods 1990 through 1994, 1995 through 1999, and 2000 and beyond. For 1990 through 1994, emissions were estimated using the most recent version of EPA's PFC Emissions Vintage Model (PEVM) (Burton & Beizaie 2001).[17] PFC emissions per square centimeter of silicon increase as the number of layers in semiconductor devices increases. Thus, PEVM incorporates information on the two attributes of semiconductor devices that affect the number of layers: (1) linewidth technology (the smallest feature size, which decreases as layers increase), and (2) product type (memory vs. logic). PEVM derives historical consumption of silicon (i.e., square centimeters) by linewidth technology from published data on annual wafer starts and average wafer size (VLSI 2003a,b,c). For each linewidth technology, a weighted average number of layers is estimated using VLSI product-specific worldwide silicon demand data in conjunction with complexity factors (i.e., the number of layers per IC) specific to product type (International SEMATECH 1998-2003). The distribution of memory/logic devices ranges over the period covered from 52 percent logic devices in 1995 to 59 percent logic devices in 2000. These figures were used to determine emission factors that express emissions per average layer per unit of area of silicon consumed during product manufacture. The per-layer emission factor was based on the total annual emissions reported by participants in EPA's PFC Reduction/Climate Partnership for the Semiconductor Industry in 1995 and later years.

For 1995 through 1999, total U.S. emissions were extrapolated from the total annual emissions reported by the Partnership participants (Burton & Lieberman 2004). The emissions reported by the participants were divided by the ratio of the total layer-weighted capacity of the plants operated by the participants and the total layer-weighted capacity of all of the semiconductor plants in the United States; this ratio represents the share of layer-weighted capacity attributable to partnership participants. The layer-weighted capacity of a plant (or group of plants) consists of the silicon capacity of that plant multiplied by the number of layers used to fabricate products at that plant. This method assumes that participants and non-participants have similar capacity utilizations and per-layer emission factors.

The U.S. estimate for the years 2000 through 2003—the period during which partners began the consequential application of PFC-reduction measures—used a different estimation method. The emissions reporting by Partnership participants for each year were accepted as the quantity emitted from the share of the industry represented by those Partners. Remaining emissions (those from non-partners), however, were estimated using PEVM and the method described above. (Non-partners are assumed not to have implemented any PFC-reduction measures, and PEVM models emissions without such measures.) The portion of the U.S. total attributed to non-Partners is obtained by multiplying PEVM's total U.S. figure by the non-partner share of total layer-weighted silicon capacity for each year (as described above). Annual updates to PEVM reflect published figures for actual silicon consumption from VLSI Research, Inc. as well as revisions and additions to the world population of semiconductor manufacturing plants.

Two different approaches were also used to estimate the distribution of emissions of specific PFCs. Before 1999, when there was no consequential adoption of PFC-reducing measures, a fixed distribution was assumed to apply to the entire U.S. industry. This distribution was based upon the average PFC purchases by semiconductor

[17] The most recent version of this model is v.3.1.0306.0304r, completed in March 2004.

manufacturers during this period and the application of IPCC default emission factors for each gas. For the 2000 through 2003 period, the 1990 through 1999 distribution was assumed to apply to the non-Partners. Partners, however, began to report gas-specific emissions during this period. Thus, gas specific emissions for 2000 through 2003 were estimated by adding the emissions reported by the Partners to those estimated for the non-Partners.

Partners estimate their emissions using a range of methods. For 2003, most participants cited a method at least as accurate as the IPCC's Tier 2c Methodology, recommended in *Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories* (IPCC 2000). The partners with relatively high emissions typically use the more accurate IPCC 2b or 2a methods, multiplying estimates of their PFC consumption by process-specific emission factors that they have either measured or obtained from tool suppliers.

Data used to develop emission estimates were prepared in cooperation with the Partnership. Estimates of operating plant capacities and characteristics for participants and non-participants were derived from the Semiconductor Equipment and Materials International (SEMI) *World Fab Watch* (formerly *International Fabs on Disk*) database (1996 to 2003). Estimates of silicon consumed by line-width from 1990 through 2003 were derived from information from VLSI Research (2003d), and the number of layers per line-width was obtained from International SEMATECH's *International Technology Roadmap: 1998 – 2003.*

Uncertainty

Quantitative uncertainty of this source category was performed using the IPCC-recommended Tier 2 uncertainty estimation methodology, Monte Carlo Stochastic Simulation technique. Uncertainty is associated with the emission estimates reported by the Partners, with the estimated share of total layer-weighted silicon capacity in 2003 attributable to the Partners, and with the total U.S. PFC emissions estimate as determined by PEVM.

The Monte Carlo analysis presented below relied on estimates of uncertainty attributed to these three variables. Estimates of uncertainty for the three variables were in turn developed using the estimated uncertainties associated with the individual inputs to each variable, error propagation analysis, and expert judgment. For the first variable, the aggregate PFC emissions data supplied to the partnership, EPA estimated an uncertainty of ±10 percent (representing a 95 percent confidence interval). This value accounts for uncertainty in partners' estimates of gas-volume usage, and was calculated using 2003 Partnership submittals. Through expert judgment and review of the emission reports submitted by companies under the Partnership agreement, the relative uncertainties were assumed to be the same for each submittal in 2003, equal to ±29 percent of the individual Partner's reported value. Under that assumption, uncertainty propagated across all Partners resulted in a combined relative uncertainty equal to about 10 percent of the aggregate emissions reports under the Partnership. For the second variable, the share of U.S. layer-weighted silicon capacity accounted for by non-Partners, an uncertainty of ±36 percent was estimated based on the variability of the share over the period 1995 through 2003.

For the third variable, the relative error associated with the PEVM estimate in 2003, EPA estimated an uncertainty of ±44 percent, using the calculus of error propagation and considering the aggregate average emission factor, world silicon consumption, the U.S. share of layer-weighted silicon capacity, and the number of layers. The uncertainty associated with the aggregate average emission factor was estimated to be 15 percent based on the variability exhibited by the emission factor from 1996 through 1999. The uncertainty associated with the U.S. share of capacity was estimated to be 10 percent based on information from the firm that compiled the database; the principal source of errors was determined to be incomplete e-mail and telephone surveys of manufacturers (SMA 2003). The uncertainty associated with silicon consumption data was estimated to be 10 percent, based on the reliability of industry surveys of world silicon consumption by technology node. Finally, the uncertainty associated with the number of layers was estimated to be 39 percent.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-75. The emissions estimate for total U.S. PFC emissions from semiconductor manufacturing were estimated to be between 3.7 and 5.7 Tg CO_2 Eq. at a 95 percent confidence level (or in 19 out of 20 Monte Carlo Stochastic Simulations). This indicates a range of 20 percent below to 23 percent above the emissions estimate of 4.6 Tg CO_2 Eq. It should be noted that this range and the associated percentages apply to the estimate of total emissions rather than those of individual gases.

Uncertainties associated with individual gases will be somewhat higher than the aggregate, but were not explicitly modeled.

Table 4-75: Tier 2 Quantitative Uncertainty Estimates for HFC, PFC, and SF_6 Emissions from Semiconductor Manufacture (Tg CO_2 Eq. and Percent)

Source	Gas	2003 Emission Estimate[a] (Tg CO_2 Eq.)	Uncertainty Range Relative to Emission Estimate[b] (Tg CO_2 Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Semiconductor Manufacture	HFC, PFC, and SF_6	4.6	3.7	5.7	-20%	+23%

[a] Because the uncertainty analysis covered all emissions (including NF_3), the emission estimate presented here does not match that shown in Table 4-73.
[b] Range of emissions estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

Planned Improvements

The method by which non-partner related emissions are estimated (i.e., PEVM) is not expected to change (with the exception of possible future updates to emission factors and added technology nodes). Future improvements to the national emission estimates will primarily be associated with determining the portion of national emissions to attribute to partner report totals (about 80 percent in recent years). As the nature of the partner reports change through time and industry-wide reduction efforts increase, consideration will be given to what emission reduction efforts—if any—are likely to be occurring at non-partner facilities (currently none are assumed to occur.)

4.20. Magnesium Production and Processing (IPCC Source Category 2C4)

The magnesium metal production and casting industry uses sulfur hexafluoride (SF_6) as a cover gas to prevent the oxidation of molten magnesium in the presence of air. A dilute gaseous mixture of SF_6 with dry air and/or CO_2 is blown over molten magnesium metal to induce and stabilize the formation of a protective crust. A small portion of the SF_6 reacts with the magnesium to form a thin molecular film of mostly magnesium oxide and magnesium fluoride. The amount of SF_6 reacting in magnesium production and processing is assumed to be negligible and thus all SF_6 used is emitted into the atmosphere. Sulfur hexafluoride has been used in this application around the world for the last twenty years. It has largely replaced salt fluxes and SO_2, which are more toxic and corrosive than SF_6.

The magnesium industry emitted 3.0 Tg CO_2 Eq. (0.1 Gg) of SF_6 in 2003 (see Table 4-76). This represents a 12 percent increase from 2002. The increase is attributable to a 1.5 percent rise in production and casting levels and to a 10.5 percent increase in the weighted-average SF_6 usage rate at these facilities. There are no significant plans for expansion of primary magnesium production in the United States, but demand for magnesium metal by U.S. casting companies has grown as auto manufacturers design more lightweight magnesium parts into vehicle models. In the last ten years, the quantity of magnesium used in North American-produced vehicles has doubled (USGS 2004a). Foreign magnesium producers are expected to meet the growing U.S. demand for primary magnesium (USGS 2004a).

Table 4-76: SF_6 Emissions from Magnesium Production and Processing (Tg CO_2 Eq. and Gg)

Year	Tg CO_2 Eq.	Gg
1990	5.4	0.2
1997	6.3	0.3
1998	5.8	0.2
1999	6.0	0.3
2000	3.2	0.1
2001	2.6	0.1

2002	2.6	0.1
2003	3.0	0.1

Methodology

Emission estimates for the magnesium industry incorporate information provided by industry participants in EPA's SF_6 Emission Reduction Partnership for the Magnesium Industry. The partnership started in 1999 and, currently, participating companies represent 100 percent of U.S. primary production and over 80 percent of the casting sector (i.e., die, gravity, wrought, and anode casting). Emissions for 1999 through 2003 from primary production, some secondary production (i.e., recycling), and a large fraction of die casting were reported by participants. The 1999 through 2003 emissions from the remaining secondary production and casting were estimated by multiplying industry emission factors (kg SF_6 per metric ton of Mg produced or processed) by the amount of metal produced or consumed in the five major processes (other than primary production) that require SF_6 melt protection: 1) secondary production; 2) die casting; 3) gravity casting; 4) wrought products; and 5) anodes. The emission factors are provided below in Table 4-77. Because only one primary producer existed in the United States in 2003, the emission factor for primary production is withheld to protect production information. However, the emission factor has not risen above the 1995 value of 1.1 kg SF_6 per metric ton.

Die casting emissions for 1999 through 2003, which accounted for 48 to 75 percent of all SF_6 emissions from U.S. casting and recycling processes during this period, were estimated based on information supplied by industry partners. From 2000 to 2003, partners accounted for all U.S. die casting that was tracked by USGS. In 1999, partners did not account for all die casting tracked by USGS, and, therefore, it was necessary to estimate the emissions of die casters who were not partners. Die casters who were not partners were assumed to be similar to partners who cast small parts. Due to process requirements, these casters consume larger quantities of SF_6 per metric ton of processed magnesium than casters that process large parts. Consequently, emissions estimates from this group of die casters were developed using an average emission factor of 5.2 kg SF_6 per metric ton of magnesium. The emission factors for the other industry sectors (i.e., secondary production, gravity, wrought, and anode casting) were based on discussions with industry representatives.

Table 4-77: SF_6 Emission Factors (kg SF_6 per metric ton of magnesium)

Year	Secondary	Die Casting	Gravity	Wrought	Anodes
1999	1	2.14[a]	2	1	1
2000	1	0.73	2	1	1
2001	1	0.77	2	1	1
2002	1	0.70	2	1	1
2003	1	0.84	2	1	1

[a] The 1999 factor is a weighted average that includes an estimated emission factor of 5.2 kg SF_6 per metric ton of magnesium for die casters that do not participate in the Partnership.

Data used to develop these emission estimates were provided by the magnesium partnership participants and the USGS. U.S. magnesium metal production (primary and secondary) and consumption (casting) data from 1990 through 2003 were available from the USGS (USGS 2002, 2003, 2004b). Emission factors from 1990 through 1998 were based on a number of sources. Emission factors for primary production were available from U.S. primary producers for 1994 and 1995, and an emission factor for die casting of 4.1 kg per metric ton was available for the mid-1990s from an international survey (Gjestland & Magers 1996).

To estimate emissions for 1990 through 1998, industry emission factors were multiplied by the corresponding metal production and consumption (casting) statistics from USGS. The primary production emission factors were 1.2 kg per metric ton for 1990 through 1993, and 1.1 kg per metric ton for 1994 through 1996. For die casting, an emission factor of 4.1 kg per metric ton was used for the period 1990 through 1996. For 1996 through 1998, the emission factors for primary production and die casting were assumed to decline linearly to the level estimated based on partner reports in 1999. This assumption is consistent with the trend in SF_6 sales to the magnesium sector that is reported in the RAND survey of major SF_6 manufacturers, which shows a decline of 70 percent from 1996 to 1999 (RAND 2002). The emission factors for the other processes (i.e., secondary production, and gravity, wrought, and anode casting), about which less is known, were assumed to remain constant at levels defined in Table 4-65.

Uncertainty

An uncertainty of 5 percent was assigned to the SF_6 emissions data reported by each participant in the SF_6 Emission Reduction Partnership. These data have low uncertainty since they are prepared through facility-specific tracking of SF_6 cylinder purchases, usage, and returns. If partners did not report emissions data during the current reporting year, SF_6 emissions data were estimated using available emission factor and production information reported in prior years. For example, to estimate 2003 emission factors, the average change in emission factor from 2002 to 2003 for reporting partners was applied to the 2002 emission factor of the non-reporting partner. The uncertainty associated with the extrapolated emission factor was assumed to be 25 percent. For production data, if estimates were unavailable for the current reporting year, data from the last reported year was applied.

For 2003, the uncertainty associated with this approach was assumed to be 30 percent. Between 1999 and 2003, non-reporting partners have accounted for between 0 and 17 percent of total estimated sector emissions. For those industry processes that are not represented in EPA's partnership, such as gravity, anode, and wrought casting, SF_6 emissions were estimated using production and consumption statistics reported by USGS and an estimated process-specific emission factor (see Table 4-78). The uncertainty associated with USGS-reported statistics and emission factors were assumed to be 25 percent and 75 percent, respectively. In general, where precise quantitative information was not available on the uncertainty of a parameter, a conservative (upper-bound) value was used.

Table 4-78: Simulated Variables for Tier 2 Uncertainty Analysis

Parameter	Probability Distribution	Uncertainty[a] (%)
Partner-Reported SF_6 Data (kg SF_6)	Normal	5
SF_6 Emission Factor for Non-Reporting Partners (kg SF_6/metric ton Mg)	Normal	25
Production Data for Non-Reporting Partners (metric ton Mg)	Normal	30
USGS Production Data for Gravity, Anode, Wrought Casting and Secondary Production (metric ton Mg)	Normal	25
SF_6 Emission Factor for Gravity, Anode, Wrought Casting and Secondary Production (kg SF_6/metric ton Mg)	Normal	75

[a] Reflects a 95 percent confidence interval.

Additional uncertainties exist in these estimates, such as the basic assumption that SF_6 neither reacts nor decomposes during use. The melt surface reactions and high temperatures associated with molten magnesium could potentially cause some gas degradation. Recent measurement studies have identified SF_6 cover gas degradation at hot-chambered die casting machines on the order of 10 percent (Bartos et al. 2003). As is the case for other sources of SF_6 emissions, total SF_6 consumption data for magnesium production and processing in the United States were not available. Sulfur hexafluoride may also be used as a cover gas for the casting of molten aluminum with high magnesium content; however, to what extent this technique is used in the United States is unknown.

A Monte Carlo analysis was applied to estimate the overall uncertainty of the emission estimate for the U.S. magnesium industry. Random variables were selected from the probability density functions for each parameter, which were assumed to be characterized by normal distributions. In the cases of estimates developed from partners and non-reporting partners, probability density functions were applied to parameters (i.e., SF_6 emissions data, emission factors and production data) at the facility-specific level. The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-79. Magnesium production and processing SF_6 emissions were estimated to be between 2.6 and 3.3 Tg CO_2 Eq. at the 95 percent confidence level (or in 19 out of 20 Monte Carlo Stochastic Simulations). This indicates a range of approximately 11 percent below to 13 percent above the emission estimate of 3.0 Tg CO_2 Eq.

Table 4-79: Tier 2 Quantitative Uncertainty Estimates for SF_6 Emissions from Magnesium Production and Processing (Tg CO_2 Eq. and Percent)

Source	Gas	2003 Emission Estimate	Uncertainty Range Relative to 2003 Emission Estimate[a]	
		(Tg CO_2 Eq.)	(Tg CO_2 Eq.)	(%)

			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Magnesium Production and Processing	SF_6	3.0	2.6	3.3	-11%	+13%

[a] Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

Recalculations Discussion

The emission estimates for 2000, 2001, and 2002 were adjusted upward slightly from the previously reported values. This revision reflects an update to historical data supplied by partnership participants and the USGS. The changes resulted in an average annual increase of less than 0.1 Tg CO_2 Eq. (4.1 percent) in SF_6 emissions from magnesium production and processing for the period 2000 through 2002.

Planned Improvements

As more work assessing the degree of cover gas degradation and associated byproducts is undertaken and published, results could potentially be used to refine the emission estimates, which currently assume (per IPCC Good Practice Guidance 2001) that all SF_6 utilized is emitted to the atmosphere. EPA-funded measurements of SF_6 in hot chamber die casting have indicated that the latter assumption may be incorrect, with observed SF_6 degradation on the order of 10 percent (Bartos et al. 2003). More recent EPA-funded measurement studies have confirmed this observation for cold chamber die casting (EPA 2004). Another issue that will be addressed in future inventories is the likely adoption of alternate cover gases by U.S. magnesium producers and processors. These cover gases, which include Am-Cover™ (containing HFC-134a) and Novec™ 612, have lower GWPs than SF_6, and tend to quickly decompose during their exposure to the molten metal. Additionally, as more companies join the partnership, in particular those from sectors not currently represented, such as gravity and anode casting, emission factors will be refined to incorporate these additional data.

[BEGIN BOX]

Box 4-1: Potential Emission Estimates of HFCs, PFCs, and SF_6

Emissions of HFCs, PFCs and SF_6 from industrial processes can be estimated in two ways, either as potential emissions or as actual emissions. Emission estimates in this chapter are “actual emissions,” which are defined by the *Revised 1996 IPCC Guidelines for National Greenhouse Gas Inventories* (IPCC/UNEP/OECD/IEA 1997) as estimates that take into account the time lag between consumption and emissions. In contrast, “potential emissions” are defined to be equal to the amount of a chemical consumed in a country, minus the amount of a chemical recovered for destruction or export in the year of consideration. Potential emissions will generally be greater for a given year than actual emissions, since some amount of chemical consumed will be stored in products or equipment and will not be emitted to the atmosphere until a later date, if ever. Although actual emissions are considered to be the more accurate estimation approach for a single year, estimates of potential emissions are provided for informational purposes.

Separate estimates of potential emissions were not made for industrial processes that fall into the following categories:

- *By-product emissions*. Some emissions do not result from the consumption or use of a chemical, but are the unintended by-products of another process. For such emissions, which include emissions of CF_4 and C_2F_6 from aluminum production and of HFC-23 from HCFC-22 production, the distinction between potential and actual emissions is not relevant.
- *Potential emissions that equal actual emissions*. For some sources, such as magnesium production and processing, no delay between consumption and emission is assumed and, consequently, no destruction of the chemical takes place. In this case, actual emissions equal potential emissions.

Table 4-80 presents potential emission estimates for HFCs and PFCs from the substitution of ozone depleting substances, HFCs, PFCs, and SF_6 from semiconductor manufacture, and SF_6 from magnesium production and processing and electrical transmission and distribution.[18] Potential emissions associated with the substitution for ozone depleting substances were calculated using the EPA's Vintaging Model. Estimates of HFCs, PFCs, and SF_6 consumed by semiconductor manufacture were developed by dividing chemical-by-chemical emissions by the appropriate chemical-specific emission factors from the IPCC Good Practice Guidance (Tier 2c). Estimates of CF_4 consumption were adjusted to account for the conversion of other chemicals into CF_4 during the semiconductor manufacturing process, again using the default factors from the IPCC Good Practice Guidance. Potential SF_6 emissions estimates for electrical transmission and distribution were developed using U.S. utility purchases of SF_6 for electrical equipment. From 1999 through 2003, estimates were obtained from reports submitted by participants in EPA's SF_6 Emission Reduction Program for Electric Power Systems. U.S. utility purchases of SF_6 for electrical equipment from 1990 through 1998 were backcasted based on world sales of SF_6 to utilities. Purchases of SF_6 by utilities were added to SF_6 purchases by electrical equipment manufacturers to obtain total SF_6 purchases by the electrical equipment sector.

Table 4-80: 2003 Potential and Actual Emissions of HFCs, PFCs, and SF_6 from Selected Sources (Tg CO_2 Eq.)

Source	Potential	Actual
Substitution of Ozone Depleting Substances	181.0	99.5
Aluminum Production	-	3.8
HCFC-22 Production	-	12.3
Semiconductor Manufacture	6.6	4.3
Magnesium Production and Processing	3.0	3.0
Electrical Transmission and Distribution	21.8	14.1

- Not applicable.

[END BOX]

4.21. Industrial Sources of Ambient Air Pollutants

In addition to the main greenhouse gases addressed above, many industrial processes generate emissions of ambient air pollutants. Total emissions of nitrogen oxides (NO_x), carbon monoxide (CO), and nonmethane volatile organic compounds (NMVOCs) from non-energy industrial processes from 1990 to 2003 are reported in Table 4-81.

Table 4-81: NO_x, CO, and NMVOC Emissions from Industrial Processes (Gg)

Gas/Source	1990		1997	1998	1999	2000	2001	2002	2003
NO_x	**591**		**629**	**637**	**595**	**626**	**656**	**630**	**648**
Chemical & Allied Product Manufacturing	152		115	117	93	95	97	95	92
Metals Processing	88		81	81	78	81	86	76	83
Storage and Transport	3		15	15	13	14	15	14	14
Other Industrial Processes	343		417	424	409	434	457	442	457
Miscellaneous*	5		1	1	2	2	1	3	2
CO	**4,124**		**3,153**	**3,163**	**2,156**	**2,217**	**2,339**	**2,308**	**2,431**
Chemical & Allied Product Manufacturing	1,074		971	981	317	327	338	306	299
Metals Processing	2,395		1,551	1,544	1,138	1,175	1,252	1,174	1,290
Storage and Transport	69		64	65	148	154	162	195	219
Other Industrial Processes	487		528	535	518	538	558	576	575
Miscellaneous*	101		38	38	35	23	30	57	49

[18] See Annex 5 for a discussion of sources of SF_6 emissions excluded from the actual emissions estimates in this report.

NMVOCs	**2,426**	**2,038**	**2,047**	**1,813**	**1,773**	**1,769**	**1,725**	**1,711**
Chemical & Allied Product Manufacturing	575	352	357	228	230	238	194	198
Metals Processing	111	71	71	60	61	65	62	65
Storage and Transport	1,356	1,205	1,204	1,122	1,067	1,082	1,093	1,069
Other Industrial Processes	364	397	402	398	412	381	369	374
Miscellaneous*	20	13	13	6	3	4	7	5

* Miscellaneous includes the following categories: catastrophic/accidental release, other combustion, health services, cooling towers, and fugitive dust. It does not include agricultural fires or slash/prescribed burning, which are accounted for under the Field Burning of Agricultural Residues source.

Note: Totals may not sum due to independent rounding.

Methodology

These emission estimates were obtained from preliminary data (EPA 2004), and disaggregated based on EPA (2003), which, in its final iteration, will be published on the National Emission Inventory (NEI) Air Pollutant Emission Trends web site. Emissions were calculated either for individual categories or for many categories combined, using basic activity data (e.g., the amount of raw material processed) as an indicator of emissions. National activity data were collected for individual categories from various agencies. Depending on the category, these basic activity data may include data on production, fuel deliveries, raw material processed, etc.

Activity data were used in conjunction with emission factors, which together relate the quantity of emissions to the activity. Emission factors are generally available from the EPA's *Compilation of Air Pollutant Emission Factors, AP-42* (EPA 1997). The EPA currently derives the overall emission control efficiency of a source category from a variety of information sources, including published reports, the 1985 National Acid Precipitation and Assessment Program emissions inventory, and other EPA databases.

Uncertainty

Uncertainties in these estimates are partly due to the accuracy of the emission factors used and accurate estimates of activity data. A quantitative uncertainty analysis was not performed.

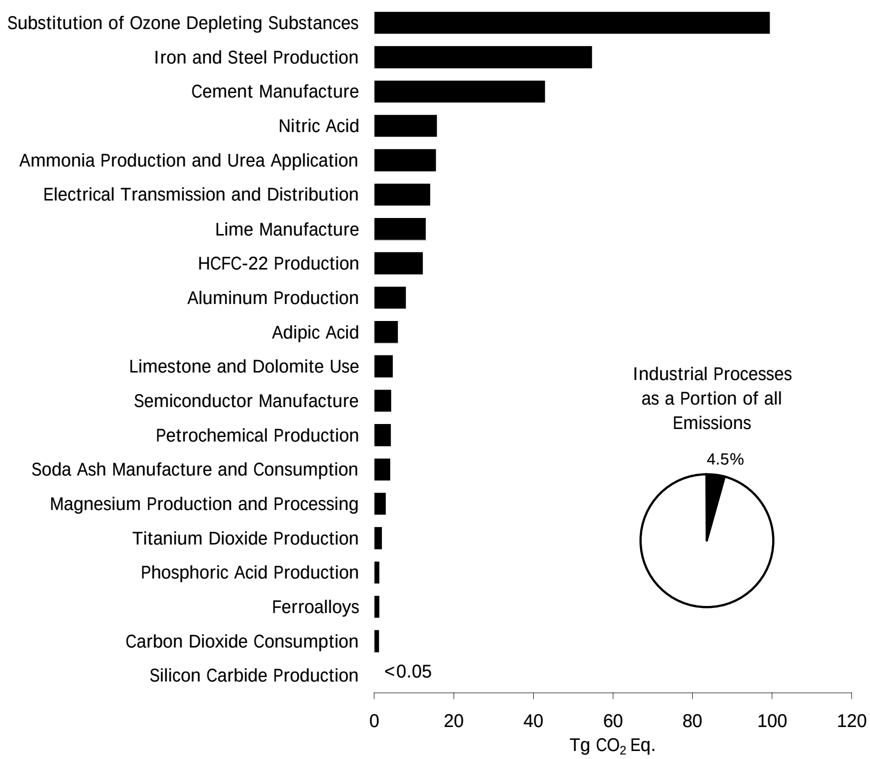

Figure 4-1: 2003 Industrial Processes Chapter Greenhouse Gas Sources